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(REV. 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

CM2000XM

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/889255

INTERNATIONAL APPLICATION NO.

PCT/US00/00794

INTERNATIONAL FILING DATE

13 January 2000

PRIORITY DATE CLAIMED

14 January 1999

TITLE OF INVENTION

**Detergent Compositions Comprising A Pectate Lyase and A Specific Surfactant System**

APPLICANT(S) FOR DO/EO/US

**SHOWELL, Michael Stanford et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
  4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. ☒ A copy of the International Application was filed (35 U.S.C. 371(c)(2))
    - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ has been transmitted by the International Bureau.
    - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b. ☐ have been transmitted by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☒ have not been made and will not be made.
  8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
  10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
  14. ☐ A substitute specification.
  15. ☒ A change of power of attorney and/or address letter.
  16. ☐ Other items or information:

"Express Mail" mailing label number

Date of Deposit

I hereby certify that this paper/fee is being deposited with the United States Postal Service "Express Mail" Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231.

Administrative Mailing Application.

Signature

EL 48362056775 650715 2CB  
13 July 2001  
*[Signature]*

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
09/889255		PCT/US00/00794		CM2000XM	
				CALCULATIONS    PTO USE ONLY	
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$710</b>	
Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20    [ ] 30    months from the earliest claimed priority date (37 CFR 1.492(e)).				<b>\$0</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	11-20 =	0	x \$18.00	<b>\$0</b>	
Independent Claims	1-3 =	0	x \$80.00	<b>\$0</b>	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			\$270.00	<b>\$0</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$710</b>	
Processing fee of \$130.00 for furnishing the English translation later than [ ] 20    [ ] 30    months from the earliest claimed priority date (37 CFR 1.492(f)).				<b>\$0</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$710</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +				<b>\$0</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$710</b>	
				Amount to be refunded	\$
				charged	\$
<p>a. [ ] A check in the amount of \$ ____ to cover the above fees is enclosed.</p> <p>b. [x] Please charge my Deposit Account No. <u>16-2480</u> in the amount of \$ <u>710</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. [x] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>16-2480</u>. A duplicate copy of this sheet is enclosed.</p> <p><b>NOTE:</b> Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p> <p><b>SEND ALL CORRESPONDENCE TO:</b></p>					
F. Taffy Customer Number 27748			<div style="text-align: center;">             Signature         </div> <div style="margin-top: 10px;"> <u>T. David Reed</u>            Name  <u>32,931</u>            Registration Number         </div>		

Case CM2000XM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Matter of:

U.S. National Phase Entry

Under 35 USC § 371 from

the International Application of :

SHOWELL, Michael Stanford et al :

Int'l Application No. PCT/US00/00794 :

Filed in the RO/US on 13 January 2000 :

Entitled: DETERGENT COMPOSITIONS COMPRISING A  
PECTATE LYASE AND A SPECIFIC  
SURFACTANT SYSTEM

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.112

Assistant Commissioner for Patents

Washington, D.C. 20231

Dear Sir:

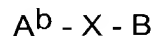
Prior to Examination and computation of the fees for entering the captioned International Application into the U.S. National Phase, please preliminarily amend the above-identified application as follows and consider the following Remarks.

AMENDMENTS

IN THE CLAIMS

Please amend Claims as follows:

1. A detergent composition comprising a pectate lyase enzyme and a surfactant selected from the group consisting of a mid-chain branched anionic surfactant, an amine oxide and/or mixture thereof wherein the mid-chain branched anionic surfactant has the formula :



wherein:

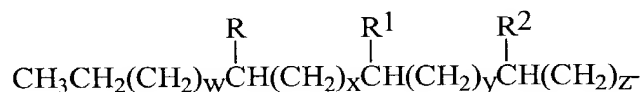
- (I)  $A^b$  is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more  $C_1 - C_3$  alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position

within the range of the position-2 carbon, counting from position 1 carbon (#1) which is attached to the - X - B moiety, to the position of the terminal carbon minus 2 carbons, (the ( $\omega$  - 2) carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the  $A^b$ -X moieties in the above formula is within the range of greater than 11 to 20;

(II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxy-propylene, alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccinates, polyalkoxyated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxyated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

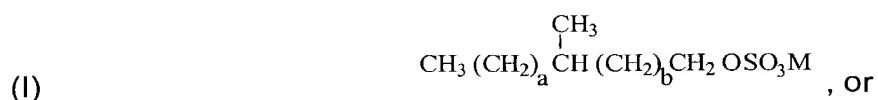
(III) X is selected from  $-CH_2-$  and  $-C(O)-$ .

2. A detergent composition according to claim 1 wherein said mid-chain branched anionic surfactant is of the above formula wherein the  $A^b$  moiety is a branched primary alkyl moiety having the formula:

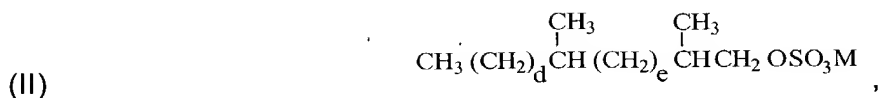


wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula, including the R,  $R^1$ , and  $R^2$  branching, is from 13 to 19; R,  $R^1$ , and  $R^2$  are each independently selected from hydrogen and  $C_1$ - $C_3$  alkyl, provided R,  $R^1$ , and  $R^2$  are not all hydrogen and, when z is 0, at least R or  $R^1$  is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and  $w + x + y + z$  is from 7 to 13.

3. A detergent composition according to claim 2 wherein said mid-chain branched anionic surfactant has the formula:

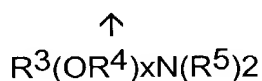






or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8; when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9; when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10; when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11; when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12; when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13; when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14; when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6; when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7; when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8; when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9; when d + e = 12, d is an integer from 2 to 11 and e is an integer from 1 to 10; when d + e = 13, d is an integer from 2 to 12 and e is an integer from 1 to 11; when d + e = 14, d is an integer from 2 to 13 and e is an integer from 1 to 12; whereby, when more than one of these sulfate surfactants is present in the surfactant system, the average total number of carbon atoms in the branched primary alkyl moieties is from 11 to 20.

4. A detergent composition according to claim 3 wherein said mid-chain branched anionic surfactant has an A<sup>b</sup> - X moiety comprising from 11 to 20 carbon atoms and B is a sulfate group.
5. A detergent composition according to claim 4 wherein said amine oxide surfactant is of the formula



wherein R<sup>3</sup> is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R<sup>4</sup> is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R<sup>5</sup> groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.


6. A detergent composition according to claim 5 wherein said amine oxide surfactant is selected from C<sub>10</sub>-C<sub>18</sub> alkyl dimethyl amine oxides; C<sub>8</sub>-C<sub>12</sub> alkoxy ethyl dihydroxy ethyl amine oxides and/or mixtures thereof.
7. A detergent composition according to claim 6 wherein said amine oxide surfactant is comprised at a level of from 0.2% to 15% by weight of total composition.
8. A detergent composition according to claim 7 wherein said mid-chain branched anionic surfactant is comprised at a level of from 0.1% to 50% by weight of the total composition.
9. A detergent composition according to claim 7 wherein said pectate lyase is present at a level of from 0.0001% to 2% pure enzyme by weight of total composition.
10. A detergent composition according to claim 1 of the present invention further comprising a pectin lyase enzyme.
11. A method of cleaning a fabric, a dishware or hard surface with a detergent composition according to claim 1, for superior cleaning performance.

REMARKS

Claims 1 thru 11 have been amended by eliminating multiple dependent claims and deleting preferably clauses. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "Version With Markings to Show Changes Made".

The support for these amendments is found in the claims as originally filed. These amendments are being entered to bring the claims into conformance with, *inter alia*, 37 CFR §1.75; no new matter is added.

Respectfully submitted,

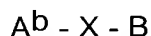
By   
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## VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the claims:

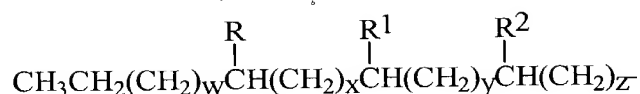
1. A detergent composition comprising a pectate lyase enzyme and a surfactant selected from the group consisting of a mid-chain branched anionic surfactant, an amine oxide and/or mixture thereof wherein the mid-chain branched anionic surfactant has the formula :



wherein:

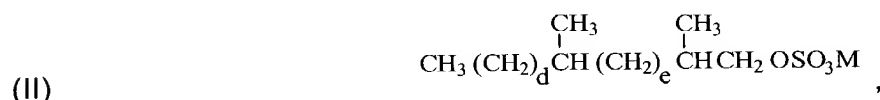
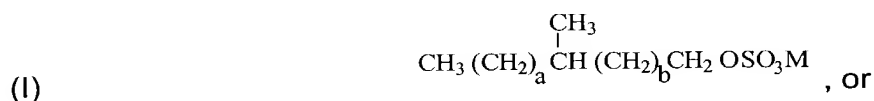
- (I)  $A^b$  is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more  $C_1 - C_3$  alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the - X - B moiety, to the position of the terminal carbon minus 2 carbons, (the  $(\omega - 2)$  carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the  $A^b$ -X moieties in the above formula is within the range of greater than 11 to 20[, preferably 14.5 to about 18, more preferably from about 15 to about 17];
- (II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxy-propylene, alkoxyated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfonates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccaminates, polyalkoxyated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxyated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkylated/polyhydroxyalkylated quats, alkylated quats, alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and
- (III) X is selected from  $-CH_2-$  and  $-C(O)-$ .

2. A detergent composition according to claim 1 wherein said mid-chain branched anionic surfactant is of the above formula wherein the  $A^b$  moiety is a branched primary alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula, including the R, R<sup>1</sup>, and R<sup>2</sup> branching, is from 13 to 19; R, R<sup>1</sup>, and R<sup>2</sup> are each independently selected from hydrogen and C<sub>1</sub>-C<sub>3</sub> alkyl[, preferably methyl,] provided R, R<sup>1</sup>, and R<sup>2</sup> are not all hydrogen and, when z is 0, at least R or R<sup>1</sup> is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

3. A detergent composition according to claim 2 [claims 1-2] wherein said mid-chain branched anionic surfactant has the formula:



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further

when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;

when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;

when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;

when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;

when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12;

when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13;

when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14;

when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;

when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;

when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8;

when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9;

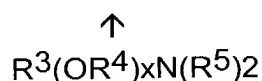
when d + e = 12, d is an integer from 2 to 11 and e is an integer from 1 to 10;

when d + e = 13, d is an integer from 2 to 12 and e is an integer from 1 to 11;

when d + e = 14, d is an integer from 2 to 13 and e is an integer from 1 to 12;

whereby, when more than one of these sulfate surfactants is present in the surfactant system, the average total number of carbon atoms in the branched primary alkyl moieties is from 11 to 20[, preferably 14.5 to 18].

4. A detergent composition according to claim 3 [claims 1-3] wherein said mid-chain branched anionic surfactant has an  $A^b - X$  moiety comprising from 11 to 20[, preferably 16 to 18] carbon atoms and B is a sulfate group.
5. A detergent composition according to claim 4 [claims 1-4] wherein said amine oxide surfactant is of the formula



wherein  $R^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each  $R^5$  is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $R^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

6. A detergent composition according to claim 5 [claims 1-5] wherein said amine oxide surfactant is selected from  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides;  $C_8$ - $C_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides and/or mixtures thereof.
7. A detergent composition according to claim 6 [claims 1-6] wherein said amine oxide surfactant is comprised at a level of from 0.2% to 15%[, preferably from 1% to 10%, more preferably less than 5%] by weight of total composition.
8. A detergent composition according to claim 7 [claims 1-7] wherein said mid-chain branched anionic surfactant is comprised at a level of from 0.1% to 50%[, preferably from 0.5% to 40%, more preferably 1% to 35%] by weight of the total composition.
9. A detergent composition according to claim 8 [any of the preceding claims] wherein said pectate lyase is present at a level of from 0.0001% to 2%[, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.02%] pure enzyme by weight of total composition.
10. A detergent composition according to claim 1 [any ]of the present invention further comprising a pectin lyase enzyme.

11. A method of cleaning a fabric, a dishware or hard surface with a detergent composition according to claim 1 [any of the preceding claims], for superior cleaning performance.

DETERGENT COMPOSITIONS COMPRISING A PECTATE LYASE AND A SPECIFIC SURFACTANT SYSTEM

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**Field of the Invention**

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The present invention relates to detergent compositions comprising a pectate lyase and specific surfactant selected from an amine oxide surfactant and/or a mid-chain branched anionic surfactant.

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**Background of the invention**

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Performance of a detergent product is judged by a number of factors, including the ability to remove soils, and the ability to prevent the redeposition of the soils, or the breakdown products of the soils on the articles in the wash. Therefore, detergent compositions include nowadays a complex combination of active ingredients which fulfil certain specific needs. In particular, current detergent formulations generally include surfactants and detergent enzymes providing cleaning and fabric care benefits.

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Removal of stains stemming from plants, wood, mould-clay based soils, muddy soils, and fruits is one of today's toughest cleaning task; especially with the trend toward low wash temperatures. These stains typically contain complex mixtures of fibrous material based mainly on carbohydrates and their derivatives : fibres and cell wall components. Plant based soils are additionally accompanied with amylose, sugars and their derivatives. Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived



from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango or broccoli soils. Indeed, pectin polymers are important constituents of plant cell walls. Pectin is a hetero-polysaccharide with a backbone composed of alternating  
5 homogalacturonan (smooth regions) and rhamnogalacturonan (hairy regions). The smooth regions are linear polymers of 1,4-linked alpha-D-galacturonic acid. The galacturonic acid residues can be methyl-esterified on the carboxyl group to a varying degree, usually in a non-random fashion with blocks of polygalacturonic acid being completely methyl-esterified. The substrates on which pectin  
10 containing stains are commonly found can be fabrics, dishware or hard surfaces.

In addition, the complex nature of everyday "body" soils typically found on pillow cases, T-shirts, collars and socks, provides a continuous thorough cleaning challenge for detergents. These soils are difficult to remove completely due in  
15 part to their interaction with the pectin components in the primary cell walls of cotton fibers comprising cotton containing fabrics, and often residues build up on such fabric leading to dinginess and yellowing. Moreover, body fluid stains, such as blood and menstrual fluids, are often difficult to remove effectively from a soiled item, especially when the stains have been aged. Everyday body soils are  
20 also found on sanitary and kitchen surfaces such as bathtubs, toilet bowls and dishware.

Amine oxide surfactants have been used since a very long time in the detergency industry and are known to provide good cleaning benefits, especially on grease /  
25 lipids soils. Anionic surfactants have been used since a very long time in the detergency industry. In recent years, mid-chain branched anionic surfactants were developed such as described in WO97/39091 and WO97/38956 and in the co-pending US applications US97/06485, US97/06474, US97/06339, US97/06476 and US97/06338. These mid-chain branched anionic surfactants  
30 are characterised by having the ability to couple with high hydrophobicity, a low temperature solubility and a high hardness tolerance. And therefore provide good cleaning properties, especially on greasy stains and body soils. These mid-chain branched are especially useful in cool or cold water laundry washing conditions, even in temperatures as low as 20°C-5°C. It has also been found that a  
35 combination of two or more of these mid-chain branched surfactants can provide

a surfactant mixture that is even higher in surfactancy and has better low temperature water solubility.

Pectin degrading enzymes are known to provide soil/stain removal benefits when used in washing and cleaning operations, specifically to provide the removal of a broad range of plant and fruit based stains and enhance the body soil cleaning profile of the detergent compositions. By pectin degrading enzyme it is meant herein any enzyme which acts to break down pectin substances and pectin related substances. Pectin degrading enzymes can be classified according to their preferential substrate, highly methyl-esterified pectin or low methyl-esterified pectin and polygalacturonic acid (pectate), and their reaction mechanism, beta-elimination or hydrolysis. Pectin degrading enzymes can be mainly endo-acting, cutting the polymer at random sites within the chain to give a mixture of oligomers, or they may be exo-acting, attacking from one end of the polymer and producing monomers or dimers. Several pectinase activities acting on the smooth regions of pectin are included in the classification of enzymes provided by the Enzyme Nomenclature (1992) such as pectate lyase (EC 4.2.2.2), pectin lyase (EC 4.2.2.10), polygalacturonase (EC 3.2.1.15), exo-polygalacturonase (EC 3.2.1.67), exo-polygalacturonate lyase (EC 4.2.2.9) and exo-poly-alpha-galacturonosidase (EC 3.2.1.82). The pectin degrading enzymes are natural mixtures of the above mentioned enzymatic activities.

Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading enzymes are specifically directed to degrade pectin substances and in particular plant cell walls. In particular, pectate lyase enzymes are directed to the cleavage of  $\alpha$ -D-(1,4) glycosidic bonds in poly-D-galacturonans by the mechanism of  $\beta$ -elimination. These pectate lyase enzymes further help as well the removal of mixed stains / soils comprising pectin substances and other components. However, soils / stains which are not sensitive to pectate lyases such as non-pectin carbohydrates, lipids, proteins and their derivatives may block the accessibility of the pectin substances to the enzymes and necessitate a further strong detergent ingredient.

It has been surprisingly found that a unique surfactant system containing a surfactant selected from an amine oxide surfactant and/or a mid-chain branched anionic surfactant, can maximise the pectate lyase enzyme cleaning efficiency. It has been surprisingly found that detergent compositions comprising a pectate lyase and such selected surfactant, provide superior cleaning due to the synergistic effect of the selected surfactant removing greasy stains and the pectate lyase degrading the pectin components of such soils and/or in a laundry context, the pectin components of the fabric that can bind or otherwise interact with such soils, making them difficult to remove. This surfactant - enzyme mixed system delivers an outstanding cleaning effect, especially on these plant-based stains and body soils. In particular, it has been surprisingly found that such removal of greasy stains, is particularly effective with mid-chain branched anionic surfactant at low temperature.

The use of pectin degrading enzymes in detergent has already been recognised in the art. The use of pectin enzyme is also recognised for the cleaning of contact lenses (US 4,710,313 - J60196724). Enzymes having a pectinase activity are described in DE 36 35 427 to increase the capacity of the detergent for removing inorganic dirt, e.g. sludges, from laundry without damaging the fibres and without discoloration to allow the use of zeolites and polycarbonate builders which have a lower capacity for dispersing inorganic materials than the phosphates. Benefits for the use of pectin enzymes in detergent formulations, particularly those designed for use in laundry, dishwashing and household cleaning operations have been recognised in WO95/25790. JP 60226599 describes detergent composition comprising conventional detergent actives and a cellulase and hydrolase such as hemicellulase, pectinase, amylase or protease. The combination of cellulase and hydrolase is said to give a good washing effect on inorganic fouling together with enzymatic activity. WO95/09909 describes an enzyme preparation comprising modified enzyme selected from the group of amylase, lipase, oxidoreductase, pectinase or hemicellulase; the modified enzyme having an improved performance due to an alkaline pH and/or increased surface activity obtained by chemical modification or amino acid substitution. Modified pectin and/or pectolytic and/or hemi-cellulolytic and/or lipolytic enzymes are applied advantageously in the papermaking industry and modified amylase and/or lipase in laundry and dishwashing.

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35 The present invention relates to detergent compositions comprising a pectate lyase and a surfactant selected from an amine oxide surfactant and/or mid-chain branched anionic surfactant, for providing superior cleaning performance.

Each type of pectin degrading enzyme has a unique profile of substrate specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading enzymes are specifically directed to degrade pectin substances and in particular  
5 plant cell walls. In particular, pectate lyase is a pectin degrading enzyme which splits the  $\alpha$ -1,4-glucoside bond of polygalacturonic acids found in pectin substances, to create a double bound between C4 and C5.

Pectate lyase enzymes further help the removal of mixed stains / soils  
10 comprising pectin substances and other components. However, soils / stains which are not sensitive to pectate lyases such as non-pectin carbohydrates, lipids, proteins and their derivatives may block the accessibility of the pectin substances to the enzyme and necessitate a further strong detergent ingredient.

15 It has been surprisingly found that a unique surfactant system comprising a surfactant selected from an amine oxide surfactant and/or mid-chain branched anionic surfactant, can maximise the pectate lyase cleaning efficiency. Such surfactants are known to provide superior cleaning, stain removal and in a laundry and/or fabric care context, whiteness maintenance and especially  
20 greasy/oily stain removal. Without wishing to be bound by theory, it is believed that the combination of an amine oxide surfactant and/or a mid-chain branched anionic surfactant with a pectate lyase enzyme, achieves high substrate specificity, high solution activity and high flexibility towards a variety of wash conditions and applications needs. It has been found that such combination  
25 leads to performance synergy in soil and stain cleaning, especially on food stains/soils and body soils.

Indeed and without wishing to be bound by theory, it is believed the synergistic cleaning benefits observed with the detergent compositions of the present  
30 invention is the result of the selected surfactant of the present invention, promoting the removal of greasy soils bound to the fabric by pectins and that the pectate lyase hydrolysing the pectin network which entraps a variety of soils species. Furthermore and without wishing to be doubt by theory, it is believed that the amine oxide and/or mid-chain branched anionic surfactants provide  
35 superior removal of hydrophobic soils such as body soils, mechanical and grease/oil, especially at low temperature, by emulsifying such soils and reducing

their melting points. The pectate lyase enzyme is believed to further aid the cleaning action by removing the pectin containing compounds found in a number of dirt, mud and plant-based soils as well as the natural pectin found on cotton fabric. The combination of improved hydrophobic soil removal with the removal of the pectin containing compounds of soils that can entrap other spoils materials is believed responsible for the synergistic, superior cleaning, whitening and stain removal observed with the detergent compositions of the present invention.

### **The Pectate Lyase enzyme**

An essential element of the detergent composition of the present invention is a pectate lyase enzyme.

Pectate lyase is classified within the classification of enzymes provided by the Enzyme Nomenclature (1992) as EC 4.2.2.2. Said enzyme is known to split the  $\alpha$ -1,4-glucoside bond of galacturonic acid found in pectin substances, creating a double bond between C4 and C5 and is substantially free for other pectin degrading activities, i.e. having less than 25%, preferably less than 15%, more preferably less than 5% by weight of the enzyme compound of other pectin degrading enzyme activities.

Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella*, *Streptomyces*, *Penicillium*, *Bacteroides*, *Thermomonospora*, *Fusarium*, *Aspergillus* and *Xanthomonas*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS 335:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. 58:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J. Bacteriol. 108:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem. Biophys. 93:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can. J. Microbiol. 26:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci. 31:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. 24:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soils.

Further suitable pectate lyases for use in the present invention are the protopectinases having an optimum reaction pH of 7.0 or higher when polygalacturonic acid is used as a substrate such as described in WO98/45393 and the pectic acid lyase having the amino acid sequence SEQ no 1 of EP 870 843 or having such amino acid sequence with one or more amino acid being deleted, added or substituted.

Preferred are the pectate lyase enzymes described in the international co-pending application PCT/DK98/00515, internationally filed on November 24, 1998, published under WO99/27084 :

- A pectate lyase comprising a first amino acid sequence consisting of seven (7) amino acid residues having the following sequence: Asn Leu Asn Ser Arg Val Pro (NLNSRVP);

- A pectate lyase which is :

- 10 i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus agaradhaerens*, DSM 8721, of at least 99%, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 27-359 of SEQ ID NO:2 of PCT/DK98/00515, or
- 15 iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived
- 20 polypeptide is at least 42% homologous with said polypeptide, or
- v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

- 25 i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus licheniformis*, ATCC 14580, of at least 99%, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 28-341 of SEQ ID NO:4 of PCT/DK98/00515, or
- iii) an analogue of the polypeptide defined in i) or ii) which is at least 45%
- 30 homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 233, and optionally also the arginine in position 238, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

5 v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

10 i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:14 of PCT/DK98/00515 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:14 of PCT/DK98/00515 higher than 97.3%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 181-509 of SEQ ID NO:6 of PCT/DK98/00515, or

15 iii) an analogue of the polypeptide defined in i) which is at least 50% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 390, and optionally also the arginine in position 395, is conserved and the derived polypeptide is at least 44% homologous with said polypeptide, or

20 v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is :

i) a polypeptide produced by the species *Bacillus halodurans*, or

25 ii) a polypeptide comprising an amino acid sequence as shown in positions 42-348 of SEQ ID NO:8 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

30 iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 40% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is

35 i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:13 of PCT/DK98/00515 or by a *Bacillus* species



having a 16S rDNA sequence homology to SEQ ID NO:13 of PCT/DK98/00515 higher than 98.1%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-335 of SEQ ID NO:10 of PCT/DK98/00515, or

5 iii) an analogue of the polypeptide defined in i) or which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 227, and optionally also the arginine in position 232, is conserved and the derived  
10 polypeptide is at least 41% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Similarly preferred is the pectate lyase enzyme described in the international co-  
15 pending application PCT/DK98/00514, internationally filed on November 24, 1998 and published under WO99/27083 and which is :

i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 28-221 of SEQ ID NO:4 of PCT/DK98/00514, or

20 iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the lysines in positions 133 and 155 and the arginine in position 158 are conserved and the  
25 derived polypeptide is at least 66% homologous with positions 60-158 of SEQ ID NO:4 of PCT/DK98/00514, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

30 More preferred pectate lyases for the purpose of the present invention are those having optimum activity at pH's >7.0 and derived from *Streptomyces fradiae*, *Streptomyces nitrosporeus*, *Erwinia carotovora*, *Bacillus sphaeroides*, *Thermomonospora fusca*, *Pseudomonas solanacearum*, *Bacteroides thetaiotaomicron*, *Fusarium solani*, *Xanthomonas campestris*, *Bacillus*  
35 *agaradhaerens*, and/or *Bacillus licheniformis*.

Most preferred pectate lyase for the purpose of the present invention is the Pectate lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721.

5 The pectate lyase is incorporated into the detergent compositions of the present invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

10 The pectate lyase of the invention, in addition to the enzyme core comprising the catalytically domain, may also contain a cellulose binding domain (CBD), the cellulose binding domain and enzyme core (the catalytically active domain) of the enzyme being operably linked. The cellulose binding domain (CBD) may exist as an integral part of the encoded enzyme, or a CBD from another origin may be introduced into the enzyme thus creating an enzyme hybrid. In this context, the  
15 term "cellulose-binding domain" is intended to be understood as defined by Peter Tomme et al. "Cellulose-Binding Domains: Classification and Properties" in "Enzymatic Degradation of Insoluble Carbohydrates", John N. Saddler and Michael H. Penner (Eds.), ACS Symposium Series, No. 618, 1996. This definition classifies more than 120 cellulose- binding domains into 10 families (I-X), and  
20 demonstrates that CBDs are found in various enzymes such as cellulases, xylanases, mannanases, arabinofuranosidases, acetyl esterases and chitinases. CBDs have also been found in algae, e.g. the red alga *Porphyra purpurea* as a non-hydrolytic polysaccharide-binding protein, see Tomme et al., op.cit. However, most of the CBDs are from cellulases and xylanases, CBDs are found  
25 at the N and C termini of proteins or are internal. Enzyme hybrids are known in the art, see e.g. WO 90/00609 and WO 95/16782, and may be prepared by transforming into a host cell a DNA construct comprising at least a fragment of DNA encoding the cellulose- binding domain ligated, with or without a linker, to a DNA sequence encoding the pectate lyase enzyme and growing the host cell to  
30 express the fused gene. Enzyme hybrids may be described by the following formula:

CBD - MR - X

wherein CBD is the N-terminal or the C-terminal region of an amino acid sequence corresponding to at least the cellulose binding domain; MR is the  
35 middle region (the linker), and may be a bond, or a short linking group preferably of from about 2 to about 100 carbon atoms, more preferably of from 2 to 40

carbon atoms; or is preferably from about 2 to about 100 amino acids, more preferably of from 2 to 40 amino acids; and X is an N-terminal or C-terminal region of the pectate lyase of the invention.

5 The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via  
10 protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability,  
15 catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant  
20 compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

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### **The selected surfactant**

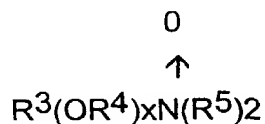
The second essential element of the detergent compositions of the present invention is a specific surfactant selected from an amine oxide being a semi-polar  
30 surfactant and/or a mid branched anionic surfactant.

#### Amine Oxide surfactant

When encompassed in the present invention, the detergent compositions of the present invention generally comprise from 0.1% to 15%, preferably from 0.1% to  
35 10%, more preferably less than 5% by weight of the total composition of such amine oxide.

Suitable amine oxides for the purpose of the present invention are described in "Surface active agent and Detergent" Volk I and II by Schwatz et al.. In particular, suitable amine oxides are the water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein  $\text{R}^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;  $\text{R}^4$  is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $\text{R}^5$  is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The  $\text{R}^5$  groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

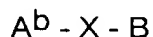
Preferred amine oxide surfactants include  $\text{C}_{10}$ - $\text{C}_{18}$  alkyl dimethyl amine oxides and  $\text{C}_8$ - $\text{C}_{12}$  alkoxy ethyl dihydroxy ethyl amine oxides.

#### The mid-chain branched surfactant

The mid-chain-branched anionic surfactants of the present invention are described in WO97/38957, WO97/39090, WO97/38956, WO97/39901 and WO97/38972 and in WO97/39091.

- 5 When encompassed in the detergent compositions of the present invention, the detergent compositions of the present invention generally comprise from 0.1% to 50%, preferably from 0.5% to 40% more preferably from 1% to 35% by weight of the total composition of one or more longer alkyl chain, mid-chain branched surfactant compounds of the formula:

10



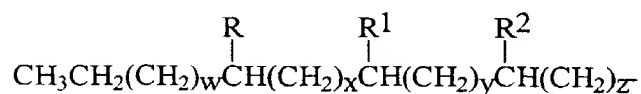
wherein:

- (I)  $A^b$  is a hydrophobic mid-chain branched alkyl moiety, having in total 9 to 22 carbons in the moiety, preferably from 12 to about 18, having: (1) a longest linear carbon chain attached to the - X - B moiety in the range of from 8 to 21 carbon atoms; (2) one or more  $C_1 - C_3$  alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of the position 2 carbon, counting from position 1 carbon (#1) which is attached to the - X - B moiety, to the position of the terminal carbon minus 2 carbons, (the  $(\omega - 2)$  carbon); and (4) when more than one of these compounds is present, the average total number of carbon atoms in the  $A^b$ -X moieties in the above formula is within the range of greater than 11 to 20, preferably 14.5 to about 18, more preferably from about 15 to about 17;
- 15 (II) B is a hydrophilic moiety selected from sulfates, sulfonates, amine oxides, polyoxyalkylene, preferably polyoxyethylene and polyoxypropylene, alkoxylated sulfates, polyhydroxy moieties, phosphate esters, glycerol sulfates, polygluconates, polyphosphate esters, phosphonates, sulfosuccinates, sulfosuccaminates, polyalkoxylated carboxylates, glucamides, taurinates, sarcosinates, glycinate, isethionates, dialkanolamides, monoalkanolamides, monoalkanolamide sulfates, diglycolamides, diglycolamide sulfates, glycerol esters, glycerol ester sulfates, glycerol ethers, glycerol ether sulfates, polyglycerol ethers, polyglycerol ether sulfates, sorbitan esters, polyalkoxylated sorbitan esters, ammonioalkanesulfonates, amidopropyl betaines, alkylated quats, alkyated/polyhydroxyalkylated quats, alkylated quats,
- 20 25 30 35

alkylated/polyhydroxylated oxypropyl quats, imidazolines, 2-yl-succinates, sulfonated alkyl esters, and sulfonated fatty acids; and

(III) X is selected from  $-\text{CH}_2-$  and  $-\text{C}(\text{O})-$ .

- 5 Preferred surfactant systems herein comprise longer alkyl chain, mid-chain branched surfactant compounds of the above formula wherein the  $\text{A}^b$  moiety is a branched primary alkyl moiety having the formula:



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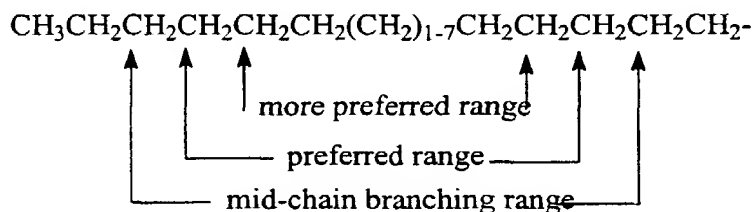
wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula (including the R,  $\text{R}^1$ , and  $\text{R}^2$  branching) is from 13 to 19; R,  $\text{R}^1$ , and  $\text{R}^2$  are each independently selected from hydrogen and  $\text{C}_1$ - $\text{C}_3$  alkyl (preferably methyl), provided R,  $\text{R}^1$ , and  $\text{R}^2$  are not all hydrogen and, when z is 0, at least R or  $\text{R}^1$  is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and  $w + x + y + z$  is from 7 to 13.

15

In general, for the mid-chain branched surfactant compounds of the surfactant system, certain points of branching (e.g., the location along the chain of the R,  $\text{R}^1$ , and/or  $\text{R}^2$  moieties in the above formula) are preferred over other points of branching along the backbone of the surfactant. The formula below illustrates the mid-chain branching range (i.e., where points of branching occur), preferred mid-chain branching range, and more preferred mid-chain branching range for mono-methyl branched alkyl  $\text{A}^b$  moieties useful according to the present invention.

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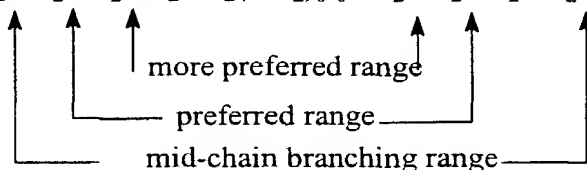


It should be noted that for the mono-methyl substituted surfactants these ranges exclude the two terminal carbon atoms of the chain and the carbon atom immediately adjacent to the  $-\text{X} - \text{B}$  group.

30

The formula below illustrates the mid-chain branching range, preferred mid-chain branching range, and more preferred mid-chain branching range for di-methyl substituted alkyl A<sup>b</sup> moieties useful according to the present invention.

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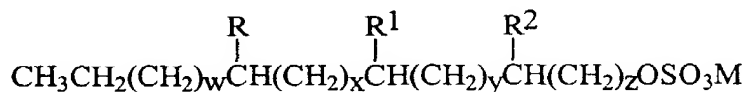
Preferred are surfactant compounds wherein in the above formula the A<sup>b</sup> moiety does not have any quaternary substituted carbon atoms (i.e., 4 carbon atoms directly attached to one carbon atom).

10

The most preferred mid-chain branched surfactants compounds for use in the detergent compositions herein are mid-chain branched primary alkyl sulfonate and, even more preferably, sulfate surfactants. It should be understood that for the purpose of the invention, it may be preferred that the surfactant system comprises a mixture of two or more mid-chain branched primary alkyl sulfate or sulphonate surfactants.

15

Preferred mid-chain branched primary alkylsulfate surfactants are of the formula



20

These surfactants have a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom) which preferably comprises from 12 to 19 carbon atoms and their branched primary alkyl moieties comprise preferably a total of at least 14 and preferably no more than 20, carbon atoms. In the surfactant system comprising more than one of these sulfate surfactants, the average total number of carbon atoms for the branched primary alkyl moieties is preferably within the range of from greater than 11 to 20, preferably 14.5 to about 17.5. Thus, the surfactant system preferably comprises at least one branched primary alkyl sulfate surfactant

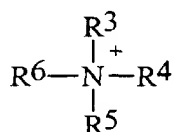
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compound having a longest linear carbon chain of not less than 12 carbon atoms or not more than 19 carbon atoms, and the total number of carbon atoms including branching must be at least 14, and further the average total number of carbon atoms for the branched primary alkyl moiety is within the range of greater than 11 to 20, preferably 14.5 to about 17.5.

R, R<sup>1</sup>, and R<sup>2</sup> are each independently selected from hydrogen and C<sub>1</sub>-C<sub>3</sub> alkyl group (preferably hydrogen or C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R<sup>1</sup>, and R<sup>2</sup> are not all hydrogen. Further, when z is 1, at least R or R<sup>1</sup> is not hydrogen.

M is hydrogen or a salt forming cation depending upon the method of synthesis. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula



wherein R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are independently hydrogen, C<sub>1</sub>-C<sub>22</sub> alkylene, C<sub>4</sub>-C<sub>22</sub> branched alkylene, C<sub>1</sub>-C<sub>6</sub> alkanol, C<sub>1</sub>-C<sub>22</sub> alkenylene, C<sub>4</sub>-C<sub>22</sub> branched alkenylene, and mixtures thereof. Preferred cations are ammonium (R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have R<sup>3</sup> equal to C<sub>1</sub>-C<sub>6</sub> alkanol, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> equal to hydrogen; dialkanol ammonium compounds of the present invention have R<sup>3</sup> and R<sup>4</sup> equal to C<sub>1</sub>-C<sub>6</sub> alkanol, R<sup>5</sup> and R<sup>6</sup> equal to hydrogen; trialkanol ammonium compounds of the present invention have R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> equal to C<sub>1</sub>-C<sub>6</sub> alkanol, R<sup>6</sup> equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:



Preferred M is sodium, potassium and the C<sub>2</sub> alkanol ammonium salts listed above; most preferred is sodium.

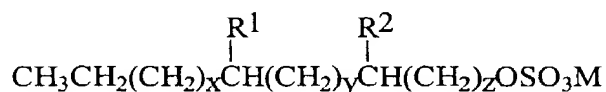


Further regarding the above formula, w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer of at least 1; and w + x + y + z is an integer from 8 to 14.

- 5 A preferred mid-chain branched primary alkyl sulfate surfactant is, a C16 total carbon primary alkyl sulfate surfactant having 13 carbon atoms in the backbone and having 1, 2, or 3 branching units (i.e., R, R<sup>1</sup> and/or R<sup>2</sup>) of in total 3 carbon atoms, (whereby thus the total number of carbon atoms is at least 16). Preferred branching units can be one propyl branching unit or three methyl branching units.

10

Another preferred surfactant system of the present invention have one or more branched primary alkyl sulfates having the formula



15

wherein the total number of carbon atoms, including branching, is from 15 to 18, and when more than one of these sulfates is present, the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 11 to 20, preferably 14.5 to about 17.5; R<sup>1</sup> and R<sup>2</sup> are each independently hydrogen or C<sub>1</sub>-C<sub>3</sub> alkyl; M is a water soluble cation; x is from 0 to 11; y is from 0 to 11; z is at least 2; and x + y + z is from 9 to 13; provided R<sup>1</sup> and R<sup>2</sup> are not both hydrogen.

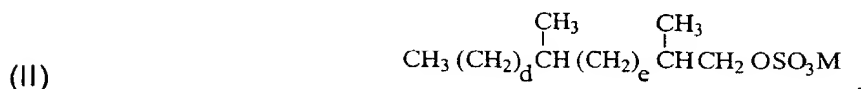
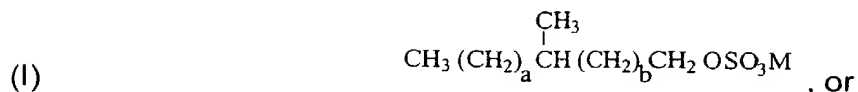
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Preferably, the surfactant system comprises at least 20% by weight of the system, more preferably at least 60% by weight, even more preferably at least 90% by weight of the system, of a mid chain branched primary alkyl sulfates, preferably having R<sup>1</sup> and R<sup>2</sup> independently hydrogen or methyl, provided R<sup>1</sup> and R<sup>2</sup> are not both hydrogen; x + y is equal to 8, 9, or 10 and z is at least 2, whereby the average total number of carbon atoms in these sulfate surfactants is preferably from 15 to 17, more preferably from 16-17.

30

Furthermore, preferred surfactant systems are those, which comprise at least about 20%, more preferably at least 60%, even more preferably at least 90% by weight of the system, of one or more mid-chain branched alkyl sulfates having the formula:

35



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further

when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;

when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;

when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;

when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;

when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12;

when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13;

when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14;

when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;

when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;

when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8;

when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9;

when d + e = 12, d is an integer from 2 to 11 and e is an integer from 1 to 10;

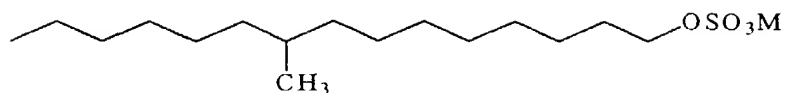
when d + e = 13, d is an integer from 2 to 12 and e is an integer from 1 to 11;

when d + e = 14, d is an integer from 2 to 13 and e is an integer from 1 to 12;

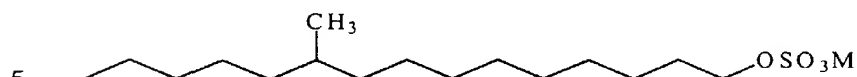
whereby, when more than one of these sulfate surfactants is present in the surfactant system, the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than 11 to 20, preferably 14.5 to about 17.5.

Preferred mono-methyl branched primary alkyl sulfates are selected from the group consisting of: 3-methyl pentadecanol sulfate, 4-methyl pentadecanol sulfate, 5-methyl pentadecanol sulfate, 6-methyl pentadecanol sulfate, 7-methyl pentadecanol sulfate, 8-methyl pentadecanol sulfate, 9-methyl pentadecanol sulfate, 10-methyl pentadecanol sulfate, 11-methyl pentadecanol sulfate, 12-methyl pentadecanol sulfate, 13-methyl pentadecanol sulfate, 3-methyl hexadecanol sulfate, 4-methyl hexadecanol sulfate, 5-methyl hexadecanol sulfate, 6-methyl hexadecanol sulfate, 7-methyl hexadecanol sulfate, 8-methyl hexadecanol sulfate, 9-methyl hexadecanol sulfate, 10-methyl hexadecanol sulfate, 11-methyl hexadecanol sulfate, 12-methyl hexadecanol sulfate, 13-

9-methylpentadecylsulfate having the formula



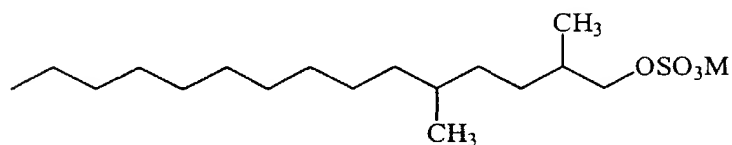
10-methylpentadecylsulfate having the formula



wherein M is preferably sodium.

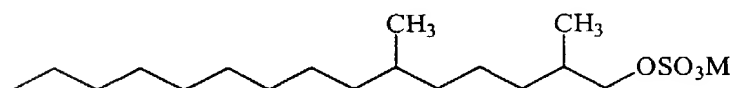
The following branched primary alkyl sulfates comprising 17 carbon atoms and having two branching units are examples of preferred branched surfactants according to the present invention:

2,5-dimethylpentadecylsulfate having the formula:

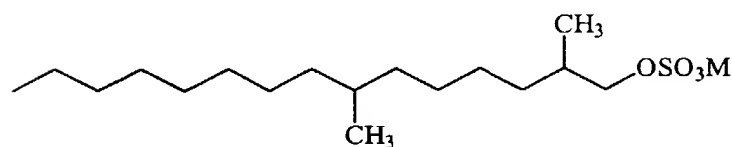


2,6-dimethylpentadecylsulfate having the formula

15

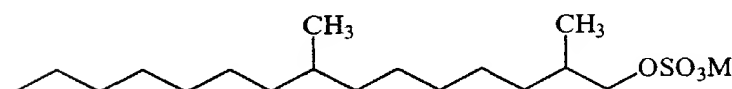


2,7-dimethylpentadecylsulfate having the formula

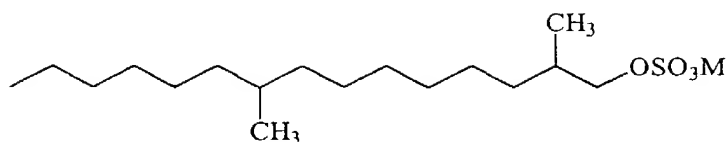


2,8-dimethylpentadecylsulfate having the formula

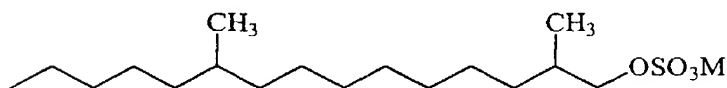
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2,9-dimethylpentadecylsulfate having the formula



2,10-dimethylpentadecylsulfate having the formula



5 wherein M is preferably sodium.

The mid-chain branched encompasses in the present invention can be manufactured according to the process described in WO97/38956. Such process prepares mid- to near mid-chain branched olefins (primarily, methyl branched at or near the mid-chain region). Such materials are then used as the basic feedstock which provides the hydrophobic portion of branched-chain deterative surfactants.

The process herein is designed to provide branched reaction products which are primarily (85%, or greater) alpha-olefins, and which are then converted into hydrophobes in the Oxo-reaction sequence noted hereinafter. Preferably, such branched alpha-olefins contain from about 11 to about 18 (avg.) total carbon atoms and comprise a linear chain having an average length in the 10-18 region. The branching is predominantly mono-methyl, but some di-methyl and some ethyl branching may occur. Advantageously, the present process results in little (1%, or less) geminal branching, i.e., little, if any, "quaternary" carbon substitution. Moreover, little (less than about 20%) vicinal branching occurs. Of course, some (ca. 20%) of the overall feedstock used in the subsequent Oxo-process may remain unbranched. Typically, and preferably from the standpoint of cleaning performance and biodegradability, the present process provides alpha-olefins with: an average number of branches (longest chain basis) in the 0.4-2.5 range; of the branched material, there are essentially no branches on carbons 1, 2 or on the terminal (omega) carbon of the longest chain of the branched material.

Following the formation and purification of the branched-chain alpha-olefin, the feedstock is subjected to an Oxo carbonylation process. In this Oxo-step, a catalyst (e.g., conventional cobalt carbonyl; see Kirk Othmer, below) which does not move the double bond from its initial position is used. This avoids the

formation of vinylidene intermediates (which ultimately yield less favorable surfactants) and allows the carbonylation to proceed at the #1 and #2 carbon atoms.

5

### **Detergent components**

The detergent compositions of the invention will preferably comprise further additional detergent components. The precise nature of these additional  
10 component, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The detergent compositions according to the invention can be liquid, paste, gels,  
15 bars, tablets, spray, foam, powder or granular. Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form. Tablet compositions can be in single phase or multiple phase form.

It has been surprisingly found that the cleaning benefits of pectate lyase enzyme can be optimised and maximised with a time controlled release technology. In  
20 particular, the time controlled technology is a tablet wherein the pectate lyase is separated from the inhibiting / deactivating other detergent ingredients in a different product phase having a different solubility in the wash. It has been surprisingly found that optimal performance efficiency of the pectate lyase enzyme can be achieved when said enzyme is incorporated into a tablet and  
25 such system delivers significant soil and stain cleaning benefits. It has further been found that such time controlled release technology allows a broader range of Pectate Lyases to be used, including those that show a high degree of instability in standard detergent matrices. Indeed, the pectate lyase and buffer materials can preferably be incorporated into the rapid dissolving portion of the  
30 tablet. Without wishing to be bound by theory, it is believed that the pectate lyase is released earlier than the inhibiting / deactivating other detergent ingredients and that optimum pectate lyase activity is obtained at the beginning of the wash under buffered conditions, allowing the formulation in detergent of pectate lyases in the full range of available pectate lyases.

35

Suitable tablets are detergent tablets which are not only sufficiently robust to withstand handling and transportation, but also at least a portion of which dissolves rapidly in the wash water providing rapid delivery of the pectate lyase enzyme. It is preferred that at least one phase of the tablet dissolves in the wash water within the first ten minutes, preferably five minutes, more preferably four minutes of the wash cycle of an automatic dishwashing or laundry washing machine. Preferably the washing machine is either an automatic dishwashing or laundry washing machine. The time within which the multi-phase tablet or a phase thereof or a detergent active component dissolves is determined according to DIN 44990 using a dishwashing machine available from Bosch on the normal 65°C washing program with water hardness at 18°H using a minimum of six replicates or a sufficient number to ensure reproducibility.

In a first embodiment, the present invention relates to laundry detergent compositions comprising a pectate lyase and a surfactant selected from an amine oxide and/or a mid-chain branched anionic surfactant (Examples 1-18). In a second embodiment, the present invention relates to dishwashing or household detergent compositions (Examples 19-23).

The compositions of the invention may for example, be formulated as hand dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics and compositions for use in general household hard surface cleaning operations. When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent





Suitable detergent compounds for use herein are selected from the group consisting of the below described compounds.

### **Surfactant system**

5

Preferably, the detergent compositions of the present invention will comprise in addition to the selected surfactant of the present invention, another surfactant system wherein the surfactant can be selected from cationic, nonionic, other anionic and/or mixtures thereof. Also suitable are ampholytic and/or zwitterionic surfactants.

10

The surfactant system comprising this selected surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of laundry detergent compositions in accord with the invention.

15

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

20

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

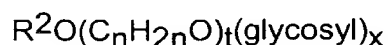
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The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic

group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

- 5 The preferred alkylpolyglycosides have the formula



10 wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To  
15 prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

20 The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight  
25 of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to  
30 condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Plurafac™ LF404 and Pluronic™ surfactants, marketed by BASF.

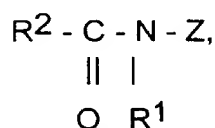
35 Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine.

The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from  
 5 about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

- 10 Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15  
 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

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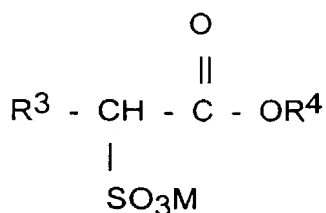


- 25 wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or  
 30 mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

- Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids  
 35 (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable

starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO<sub>3</sub>M wherein R preferably is a C<sub>10</sub>-C<sub>24</sub> hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C<sub>10</sub>-C<sub>20</sub> alkyl component, more preferably a C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C<sub>12</sub>-C<sub>16</sub> are preferred for lower wash temperatures (e.g. below about 50°C) and C<sub>16</sub>-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated

polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, 5 alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C<sub>6</sub>-C<sub>12</sub> diesters), acyl 10 sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>k</sub>-CH<sub>2</sub>COO-M<sup>+</sup> wherein R is a C<sub>8</sub>-C<sub>22</sub> alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and 15 hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also 20 generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

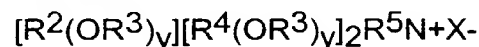
When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 25 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)<sub>m</sub>SO<sub>3</sub>M wherein R is an unsubstituted C<sub>10</sub>-C<sub>24</sub> alkyl or hydroxyalkyl group having a C<sub>10</sub>-C<sub>24</sub> alkyl 30 component, preferably a C<sub>12</sub>-C<sub>20</sub> alkyl or hydroxyalkyl, more preferably C<sub>12</sub>-C<sub>18</sub> alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or 35 substituted-ammonium cation. Alkyl ethoxyated sulfates as well as alkyl propoxyated sulfates are contemplated herein. Specific examples of substituted

ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(1.0)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate (C<sub>12</sub>-C<sub>18</sub>E(2.25)M), C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(3.0)M), and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate (C<sub>12</sub>-C<sub>18</sub>E(4.0)M), wherein M is conveniently selected from sodium and potassium.

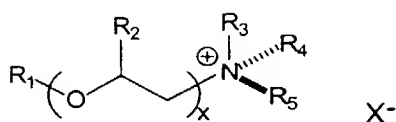
The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



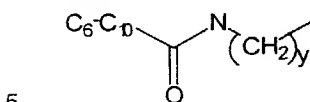
wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-CHOHCOR<sup>6</sup>CHOHCH<sub>2</sub>OH wherein R<sup>6</sup> is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :



5

Formula II

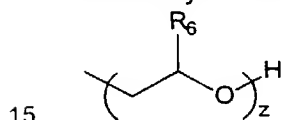
y is 2-4, preferably 3.

whereby R2 is H or a C1-C3 alkyl,

10 whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxyated alkyl of the formula III,

whereby X<sup>-</sup> is a counterion, preferably a halide, e.g. chloride or methylsulfate.



15

Formula III

R6 is C1-C4 and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

20 R1 is C8, C10 or mixtures thereof, x=0,

R3, R4 = CH3 and R5 = CH2CH2OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :

25 R1R2R3R4N<sup>+</sup>X<sup>-</sup> (i)

wherein R1 is C8-C16 alkyl, each of R2, R3 and R4 is independently C1-C4 alkyl, C1-C4 hydroxy alkyl, benzyl, and -(C2H4O)xH where x has a value from 2 to 5, and X is an anion. Not more than one of R2, R3 or R4 should be benzyl.



The preferred alkyl chain length for R<sub>1</sub> is C<sub>12</sub>-C<sub>15</sub> particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R<sub>2</sub>R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and the anion X

5 may be selected from halide, methosulphate, acetate and phosphate ions. Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- coconut trimethyl ammonium chloride or bromide;
- coconut methyl dihydroxyethyl ammonium chloride or bromide;
- 10 decyl triethyl ammonium chloride;
- decyl dimethyl hydroxyethyl ammonium chloride or bromide;
- C<sub>12</sub>-15 dimethyl hydroxyethyl ammonium chloride or bromide;
- coconut dimethyl hydroxyethyl ammonium chloride or bromide;
- myristyl trimethyl ammonium methyl sulphate;
- 15 lauryl dimethyl benzyl ammonium chloride or bromide;
- lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;
- choline esters (compounds of formula (i) wherein R<sub>1</sub> is

20  $\text{CH}_2\text{-CH}_2\text{-O-C-C}_{12-14} \text{ alkyl and R}_2\text{R}_3\text{R}_4 \text{ are methyl).}$



di-alkyl imidazolines [compounds of formula (i)].

25 Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

Typical cationic fabric softening components include the water-insoluble  
30 quaternary-ammonium fabric softening actives or the corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

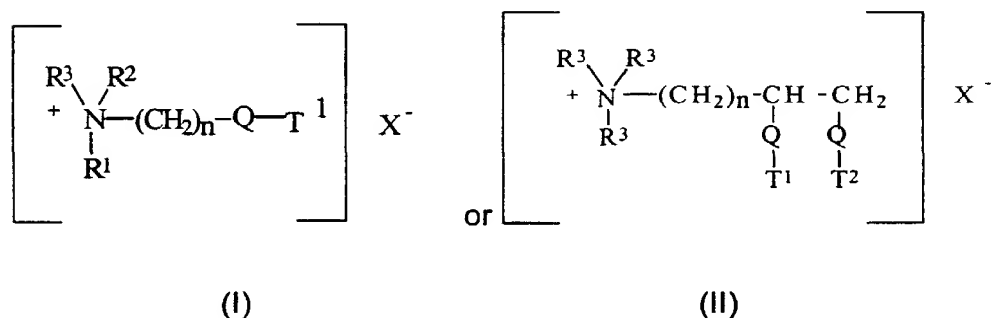
- 1) ditallow dimethylammonium chloride (DTDMAC);
- 35 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;

- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 5 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C<sub>12-14</sub> alkyl hydroxyethyl dimethylammonium chloride;
- 11) C<sub>12-18</sub> alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 10 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

15 Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

20

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



25

wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR<sup>4</sup>-C(O)-, -C(O)-NR<sup>4</sup>-;

30 R<sup>1</sup> is (CH<sub>2</sub>)<sub>n</sub>-Q-T<sup>2</sup> or T<sup>3</sup>;

R<sup>2</sup> is (CH<sub>2</sub>)<sub>m</sub>-Q-T<sup>4</sup> or T<sup>5</sup> or R<sup>3</sup>;

R<sup>3</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl or H;

R<sup>4</sup> is H or C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl;

T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> are independently C<sub>11</sub>-C<sub>22</sub> alkyl or alkenyl;

n and m are integers from 1 to 4; and

5 X<sup>-</sup> is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T<sup>1</sup>, T<sup>2</sup>, T<sup>3</sup>, T<sup>4</sup>, T<sup>5</sup> represents the mixture of long chain materials typical for tallow are particularly preferred.

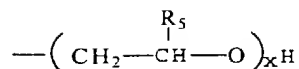
Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 15 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
  - 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
  - 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
  - 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
  - 20 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
  - 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
  - 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
  - 25 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;
- and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or



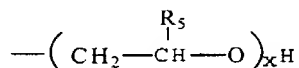


R<sub>3</sub> is either a C<sub>6</sub>-C<sub>12</sub>, preferably C<sub>6</sub>-C<sub>10</sub> alkyl chain, or R<sub>3</sub> is R<sub>4</sub>X(CH<sub>2</sub>)<sub>n</sub>, whereby X is -O-, -C(O)NH- or -NH-, R<sub>4</sub> is a C<sub>4</sub>-C<sub>12</sub>, n is between 1 to 5, preferably 2-3. R<sub>5</sub> is H or C<sub>1</sub>-C<sub>2</sub> alkyl and x is between 1 to 6.

- 5 R<sub>3</sub> and R<sub>4</sub> may be linear or branched; R<sub>3</sub> alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

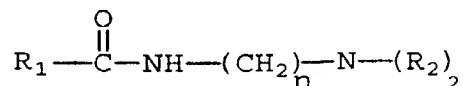
Preferred tertiary amines are R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>N where R<sub>1</sub> is a C<sub>6</sub>-C<sub>12</sub> alkyl chain, R<sub>2</sub> and R<sub>3</sub> are C<sub>1</sub>-C<sub>3</sub> alkyl or

10



where R<sub>5</sub> is H or CH<sub>3</sub> and x = 1-2.

Also preferred are the amidoamines of the formula:



15

wherein R<sub>1</sub> is C<sub>6</sub>-C<sub>12</sub> alkyl; n is 2-4, preferably n is 3; R<sub>2</sub> and R<sub>3</sub> is C<sub>1</sub>-C<sub>4</sub>

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C<sub>8</sub>-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyl-dimethylamine, C<sub>8</sub>-10 amidopropyl-dimethylamine and C<sub>10</sub> amidopropyl-dimethylamine.

25

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

30

**Bleaching agent**

The detergent compositions of the present invention can further comprise a bleaching agent such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

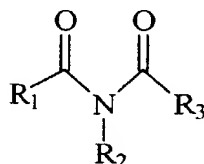
The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyl-oxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to

improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Co-pending European Patent Application No. 91870207.7 and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



wherein R<sub>1</sub> is a C<sub>7</sub>-C<sub>13</sub> linear or branched chain saturated or unsaturated alkyl group, R<sub>2</sub> is a C<sub>1</sub>-C<sub>8</sub>, linear or branched chain saturated or unsaturated alkyl group and R<sub>3</sub> is a C<sub>1</sub>-C<sub>4</sub> linear or branched chain saturated or unsaturated alkyl group.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

### ***Builder system***

The detergent compositions of the present invention can further comprise a builder. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl



carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, 5 lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates 10 disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British 15 Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan 20 - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343. 25 Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered 30 silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Other preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

- 5 Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, 10 such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

- Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 15 30% to 60% by weight.

### ***Conventional detergent enzymes***

- 20 The detergent compositions can in addition to the pectate lyase enzyme further comprise one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits, preferably a pectin lyase enzyme.

- Said enzymes include enzymes selected from cellulases, hemicellulases, 25 peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, other pectinases, keratanases, reductases, oxidases, phenoloxidases, lipxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof. A preferred 30 combination is a detergent composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

- Each type of pectin degrading enzyme has a unique profile of substrate 35 specificity, activity and stability under different hardness, pH, temperature, surfactant and other detergent ingredient matrix conditions. Pectin degrading

enzymes are specifically directed to degrade pectin substances and in particular plant cell walls. In particular, pectate lyase enzymes are specifically directed to pectic acid chains of plant cell walls such as low methoxy pectins while pectin lyase is more specifically directed towards esterified pectin chains such as high methoxyl pectins. Moreover, it has been found that pectate lyases are metal and especially calcium sensitive, whereas pectin lyases do not require metals for stabilisation and optimum enzymatic activity. It has been surprisingly found that a wide range of range of substrate specificity and a high flexibility toward a variety of wash conditions can be achieved with combining further the pectate lyase of the present invention with a pectin lyase. This results in synergistic cleaning and especially plant-based soil / stains and body soil removal.

Pectin lyase enzyme is classified under the EC classification EC 4.2.2.10, is preferably substantially free of other pectic enzymes, and acts on the pectic acids to bring about non-hydrolytic cleavage of alpha-1-4 glycosidic linkages to give oligosaccharides with terminal 4-deoxy-6- $\alpha$ -D-galacto-enuronosyl groups. The pectin lyase of the present invention is substantially free of other pectic enzymes. By "substantially free of other pectic enzymes", it is meant pectin lyase enzyme-containing compositions which contain less than 25% of pectic enzymes which are not pectin lyase enzymes, preferably less than 15%, more preferably less than 5%. The enzymatic activity can be measured according to the "Assay of trans-eliminase activities toward pectin and pectic acid" described by K. Horikoshi in Agr. Biol. Chem, Vol 36(2), 286.

Preferred pectin lyase for the purpose of the present invention is the pectin lyase described in the co-pending international patent application PCT/DK98/00514, internationally filed on November 24, 1998 and published under WO99/27083 and which is

- i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or
- ii) a polypeptide comprising an amino acid sequence as shown in positions 31-494 of SEQ ID NO:2 of PCT/DK98/00514, or
- iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or
- iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginins in positions 377 and 383 relative

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are

also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-

methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at  
5 levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent  
10 usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano  
15 Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp.,  
20 U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup>(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258  
25 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-  
30 88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Amylases ( $\alpha$  and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes detergent compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in detergent compositions include both  $\alpha$ - and  $\beta$ -amylases.  $\alpha$ -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial  $\alpha$ -amylases products are Purafect Ox Am<sup>®</sup> from Genencor and Termamyl<sup>®</sup>, Ban<sup>®</sup>, Fungamyl<sup>®</sup> and Duramyl<sup>®</sup>, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases :  $\alpha$ -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the





stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

### ***Colour care and fabric care benefits***

Technologies which provide a type of colour care benefit can also be included. Examples of these technologies are metallo catalysts for colour maintenance. Such metallo catalysts are described in co-pending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer (PCT/US97/16546) for colour care treatment and perfume substantivity are further examples of colour care / fabric care technologies and are described in the co-pending Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to

the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

## 5 ***Chelating Agents***

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates,  
10 polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

15 Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and  
20 ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis  
25 (methylenephosphonates) as DEQUEST. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are  
30 dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

- 5 If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

10 ***Suds suppressor***

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms  
15 exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a  
20 liquid carrier and applied by spraying on to one or more of the other components. A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is  
25 DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

- 30 Such suds suppressor system are described in co-pending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in co-pending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as  
35 Aerosil<sup>R</sup>.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

5 **Others**

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-  
10 encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials  
15 comprise dextrans derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating  
20 material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

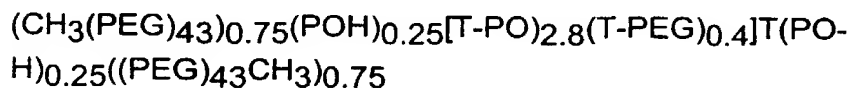
Antiredeposition and soil suspension agents suitable herein include cellulose  
25 derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the  
30 maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

35 Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2'

disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-sodium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners disclosed in EP 753 567.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is  $-(\text{OC}_2\text{H}_4)_n\text{O}-$ , PO is  $(\text{OC}_3\text{H}_6\text{O})$  and T is  $(\text{pCOC}_6\text{H}_4\text{CO})$ .

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer

capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfo benzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well-known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula  $-(CH_2CH_2O)_m(CH_2)_nCH_3$  wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

### ***Dispersants***

The detergent composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals

separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

- 5 Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the detergent compositions of the present invention.

- 10 The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

- 15 A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for  
20 example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to  
25 sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm  $\text{CaCO}_3$  (Ca:Mg=3:2) equivalent hardness.

- 30 Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

- Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include  $\text{C}_{16}$ - $\text{C}_{18}$  dimethyl amine oxide,  $\text{C}_{12}$ - $\text{C}_{18}$  alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly  $\text{C}_{12}$ - $\text{C}_{15}$  alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3  
35 (LSDP=4), and the  $\text{C}_{14}$ - $\text{C}_{15}$  ethoxylated alcohols with an average degree of

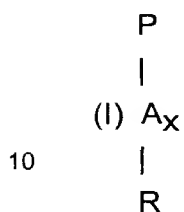


35 Addition of such polymers also enhances the performance of the enzymes according to the invention.

## a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :

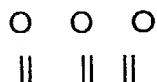
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wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

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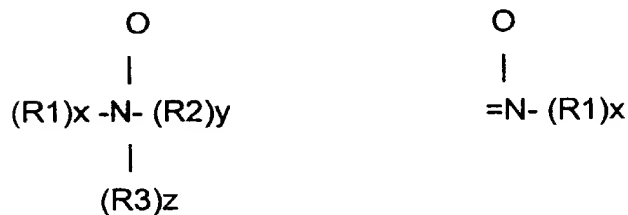
A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

20

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :

25



30

wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

35

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably

from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

#### b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

## c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

## d) Polyvinylloxazolidone :

The detergent compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

## e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

## f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039. In one embodiment, the cross-linked polymers are made in such a way that they

form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9

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### **Method of washing**

10 The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

15 The process described herein comprises contacting fabrics, dishware or any other hard surface with a cleaning solution in the usual manner and exemplified hereunder. A conventional laundry method comprises treating soiled fabric with an aqueous liquid having dissolved or dispensed therein an effective amount of the laundry detergent and/or fabric care composition. A preferred machine dishwashing method comprises treating soiled articles with an aqueous liquid  
20 having dissolved or dispensed therein an effective amount of the machine dishwashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a wash volume from 3-10 litres. According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the dishwashing  
25 composition, typically from 0.5-20g (per 25 dishes being treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition. A conventional hard surface method comprises treating soiled hard items/surfaces with e.g. a sponge, brush, cloth, etc. with an  
30 aqueous liquid having dissolved or dispensed therein an effective amount of the hard surface cleaner and/or with such composition undiluted. It also encompasses the soaking of a hard item in a concentrated solution or in a large volume of dilute solution of the detergent composition.

35 The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to

AO	: C12-14 alkyl dimethyl amine oxide
LAS	: Sodium linear C <sub>11-13</sub> alkyl benzene sulphonate.
MLAS	: Mid-chain branched alkyl benzene sulfonate
TAS	: Sodium tallow alkyl sulphate.
C <sub>xy</sub> AS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> alkyl sulfate.
C <sub>xy</sub> SAS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> secondary (2,3) alkyl sulfate.
MBAS x,y	: Sodium mid-chain branched alkyl sulfate having an average of x carbon atoms, whereof an average of y carbon atoms are comprised in (a) branching unit(s) .
C <sub>xy</sub> Ez	: C <sub>1x</sub> - C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide.
C <sub>xy</sub> EzS	: C <sub>1x</sub> - C <sub>1y</sub> sodium alkyl sulfate condensed with an average of z moles of ethylene oxide.
C <sub>x</sub> EO <sub>y</sub>	: C <sub>y</sub> alcohol with an average of ethoxylation of y.
QAS	: R <sub>2</sub> .N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> -C <sub>14</sub> .
SADS	: Sodium C <sub>14</sub> -22 alkyl disulfate of the formula 2-R.C <sub>4</sub> H <sub>7</sub> .-1,4-(SO <sub>4</sub> )-2 where R = C <sub>10</sub> -18.
MES	: x-sulpho methyl ester of C <sub>18</sub> fatty acid.
APA	: C <sub>8-10</sub> amido propyl dimethyl amine.
Soap	: Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids.
Neodol xy-z	: C <sub>1x</sub> -C <sub>1y</sub> linear primary alcohol z ethoxylate.

Nonionic	: Mixed ethoxylated/propoxylated fatty alcohol e.g. Plurafac LF404 being an alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
CFAA	: C <sub>12</sub> -C <sub>14</sub> alkyl N-methyl glucamide.
TFAA	: C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide.
TPKFA	: C <sub>12</sub> -C <sub>14</sub> topped whole cut fatty acids.
Silicate	: Amorphous Sodium Silicate (SiO <sub>2</sub> :Na <sub>2</sub> O ratio = 1.6-3.2:1).
Zeolite A	: Hydrated Sodium Aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> . 27H <sub>2</sub> O having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
(Na-)SKS-6	: Crystalline layered silicate of formula δ-Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> .
Citrate	: Tri-sodium citrate dihydrate.
Citric	: Anhydrous citric acid.
Borate	: Sodium borate
Carbonate	: Anhydrous sodium carbonate.
Bicarbonate	: Sodium hydrogen carbonate.
Sulphate	: Anhydrous sodium sulphate.
STPP	: Sodium tripolyphosphate.
TSPP	: Tetrasodium pyrophosphate.
MA/AA	: Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000.
MA/AA 1	: Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000.
AA	: Sodium polyacrylate polymer of average molecular weight 4,500.
PAAC	: Pentaamine acetate cobalt(III) salt.
PB1	: Anhydrous sodium perborate monohydrate.
PB4	: Sodium perborate tetrahydrate of nominal formula NaBO <sub>3</sub> .4H <sub>2</sub> O.
Percarbonate	: Anhydrous sodium percarbonate of nominal formula 2.74 Na <sub>2</sub> CO <sub>3</sub> .3H <sub>2</sub> O <sub>2</sub> .
TAED	: Tetraacetyl ethylene diamine.



<b>NOBS</b>	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
<b>NACA-OBS</b>	: (6-nonamidocaproyl) oxybenzene sulfonate.
<b>DOBS</b>	: Decanoyl oxybenzene sulfonate in the form of the sodium salt.
<b>DTPA</b>	: Diethylene triamine pentaacetic acid.
<b>HEDP</b>	: 1,1-hydroxyethane diphosphonic acid.
<b>DETPMP</b>	: Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060.
<b>EDDS</b>	: Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt
<b>Chelant</b>	: Chelant selected from EEDS, HEDP, DTPA, DETPMP and/or mixtures thereof.
<b>Photoactivated Bleach</b>	: Sulfonated zinc phtalocyanine encapsulated in dextrin soluble polymer.
<b>Photoactivated Bleach 1</b>	: Sulfonated alumino phtalocyanine encapsulated in dextrin soluble polymer.
<b>Pectate lyase</b>	: Pectate lyase from <i>Bacillus agaradhaerens</i> , NCIMB 40482 or DSM 8721
<b>Protease</b>	: Proteolytic enzyme sold under the tradename Savinase , Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
<b>Amylase</b>	: Amylolytic enzyme sold under the tradename Purafact Ox Am <sup>R</sup> described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl <sup>®</sup> , Fungamyl <sup>®</sup> and Duramyl <sup>®</sup> , all available from Novo Nordisk A/S and those described in WO95/26397 (sold under the tradename Natalase By Novo Nordisk).
<b>Lipase</b>	: Lipolytic enzyme sold under the tradename Lipolase Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
<b>Cellulase</b>	: Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.

Pectin lyase	: Pectin lyase produced by <i>Bacillus licheniformis</i> , ATCC 14580.
CMC	: Sodium carboxymethyl cellulose.
PVNO	: Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.
PVPVI	: Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
Silicone antifoam	: Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
Suds Suppressor	: 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form.
Opacifier	: Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621.
SRP 1	: Anionically end capped poly esters.
SRP 2	: Diethoxylated poly (1,2 propylene terephthalate) short block polymer.
QEA	: $\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) - \text{N}^+ - \text{C}_6\text{H}_{12} - \text{N}^+ - (\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O}) - (\text{C}_2\text{H}_4\text{O}))_n$ , wherein $n =$ from 20 to 30.
HMWPEO	: High molecular weight polyethylene oxide.
PEGX	: Polyethylene glycol, of a molecular weight of $x$ .
PEO	: Polyethylene oxide, with an average molecular weight of 5,000.
TEPAE	: Tetraethylenepentaamine ethoxylate.
Paraffin	: Paraffin oil sold under the tradename Winog 70 by Wintershall.
BTA	: Benzotriazole
pH	: Measured as a 1% solution in distilled water at 20°C.

Example 1

The following high density and bleach-containing laundry detergent compositions were prepared according to the present invention:

	I	II	III	IV	V	VI
Blown Powder						
Zeolite A	12.0	-	15.0	12.0	-	15.0
Sulfate	-	5.0	-	-	5.0	-
LAS	1.0	-	2.0	-	-	-
MLAS	2.0	8.0	1.0	-	-	-
MBAS 16.5,1.9	-	-	-	3.0	1.0	3.0
C45AS	3.0	2.0	4.0	3.0	2.0	4.0
QAS	-	-	1.5	-	-	1.5
DETPMP	0.4	0.4	0.4	0.4	0.4	0.4
CMC	0.4	0.4	0.4	0.4	0.4	0.4
MA/AA	1.0	2.0	2.0	1.0	2.0	2.0
Agglomerates						
AO	0.5	1.0	0.5	0.5	1.0	0.5
QAS	1.0	-	-	1.0	-	-
LAS	-	2.0	7.0	-	2.0	7.0
TAS	2.0	2.0	1.0	2.0	2.0	1.0
Silicate	3.0	-	4.0	3.0	-	4.0
Zeolite A	8.0	8.0	8.0	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0	8.0	8.0	4.0
Agglomerate						
NaSKS-6	15.0	12.0	5.0	15.0	12.0	5.0
LAS	8.0	7.0	4.0	8.0	7.0	4.0
Spray On						
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
C25E3	2.0	-	2.0	2.0	-	2.0
Dry additives						
QEA	1.0	0.5	0.5	1.0	0.5	0.5
Citric/Citrate	5.0	-	2.0	5.0	-	2.0
Bicarbonate	-	3.0	-	-	3.0	-
Carbonate	8.0	15.0	10.0	8.0	15.0	10.0
TAED and/ or NACA-OBS	6.0	-	5.0	6.0	-	5.0

	I	II	III	IV	V	VI
NOBS	-	2.0	-	-	2.0	-
Percarbonate/ PB1	14.0	7.0	10.0	14.0	7.0	10.0
Polyethylene oxide of MW 5,000,000	-	-	0.2	-	-	0.2
Bentonite clay	-	-	10.0	-	-	10.0
Citric acid	4.0	-	1.5	4.0	-	1.5
Pectin lyase	-	-	0.001	-	-	0.002
Pectate lyase	0.001	0.02	0.01	0.001	0.02	0.01
Protease	0.033	0.033	0.033	0.033	0.033	0.033
Lipase	0.008	0.008	0.008	0.008	0.008	0.008
Amylase	0.001	0.001	0.001	0.001	0.001	0.001
Cellulase	0.0014	0.0014	0.0014	0.0014	0.0014	0.0014
Silicone antifoam	5.0	5.0	5.0	5.0	5.0	5.0
Sulfate	-	3.0	-	-	3.0	-
Density (g/litre)	850	850	850	850	850	850
Moisture and miscellaneous	Up to 100%					

Example 2

- 5 The following laundry compositions, which may be in the form of granules or tablet, were prepared according to the present invention.

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	2.0	3.0	2.0	3.0
MBAS 16.5,1.9	4.0	3.0	4.0	1.0	5.0
LAS	4.0	-	4.0	-	2.0
MLAS	-	-	-	-	-
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0

	I	II	III	IV	V
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.033	0.033	0.033	0.033	0.033
Lipase	0.008	0.008	0.008	0.008	0.008
Amylase	0.001	0.001	0.002	0.001	0.001
Cellulase	0.0014	0.0014	0.0014	0.0014	.0014
Pectate lyase	0.001	0.002	0.02	0.05	0.005
Pectin lyase	-	-	0.002	-	-
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

Moisture and miscellaneous Up to 100%

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO<sub>4</sub> / PVPVI/ Suds suppressor /PEG.

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### Example 3

The following laundry compositions, which may be in the form of granules or tablet, were prepared according to the present invention.

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	4.0	3.0	3.0	3.0
MBAS 16.5,1.9	-	-	-	-	-
LAS	2.0	-	2.0	-	3.0

	I	II	III	IV	V
MLAS	6.0	-	5.0	-	4.0
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
AO	0.5	1.0	1.0	0.5	0.5
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.033	0.033	0.033	0.033	0.033
Lipase	0.008	0.008	0.008	0.008	0.008
Amylase	0.001	0.001	0.002	0.001	0.001
Cellulase	0.0014	0.0014	0.0014	0.0014	.0014
Pectate lyase	0.001	0.002	0.02	0.05	0.005
Pectin lyase	-	-	0.001	-	0.003
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

**Example 4**

The following high density laundry detergent compositions were prepared according to the present invention:

	I	II	III
Agglomerate			
QAS	2.0	-	1.0
MES	-	2.0	-
LAS	6.0	-	-
TAS	-	2.0	-
C45AS	6.0	2.0	2.0
MBAS16.5, 1.9	4.0	2.0	1.0
Zeolite A	15.0	6.0	-
Carbonate	4.0	8.0	4.0
MA/AA	4.0	2.0	-
CMC	0.5	0.5	-
DETPMP	0.4	0.4	-
Spray On			
C25E3	1.0	1.0	-
Perfume	0.5	0.5	0.5
Agglomerate			
SKS-6	7.0	15.0	20.0
LAS	5.8	9.0	15.0
Zeolite	-	0.9	-
Water	0.08	0.1	-
Dry Adds			
EDDS/HEDP	0.5	0.3	0.5
NaSKS 6 (I)	5.0	6.0	4.0
Citrate	-	1.0	-
Citric	2.0	-	2.0
NACA-OBS	4.1	-	5.0
TAED	0.8	2.0	-
Percarbonate	20.0	20.0	15.0
SRP 1	0.3	0.3	-
Pectate lyase	0.002	0.01	0.03
Protease	0.046	0.046	0.033
Lipase	0.008	0.008	0.006
Cellulase	0.0014	0.0014	0.001
Amylase	0.01	0.01	-

	I	II	III
QEA	1.0	-	1.0
Silicone antifoam	1.0	0.5	0.5
Brightener 1	0.2	0.2	-
Brightener 2	0.2	-	0.2
Density (g/litre)	850	850	800
Moisture and miscellaneous		Up to 100%	

### Example 5

- 5 The following laundry compositions, which may be in the form of granules or tablet, were prepared in accordance with the invention:

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	1.0	-	-	-	6.0
MLAS	7.0	-	8.0	-	1.0
C25AE3S	0.5	2.0	1.0	-	-
LAS/NaSKS-6	5.0	17.0	9.0	20.0	15.0
C25AE5/AE3	2.0	-	5.0	2.0	2.0
AO	0.5	0.5	0.3	0.5	1.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	10.0	10.0	-	10.0
SKS-6	-	-	2.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
PC	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-



	I	II	III	IV	V
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.046	0.046	0.033	0.033	0.033
Lipase	0.008	0.008	0.006	0.008	0.008
Cellulase	0.001	0.001	0.001	0.001	0.001
	4	4			
Amylase	0.001	0.001	-	.0014	.0014
Pectate lyase	0.001	0.02	0.01	0.015	0.03
Pectin lyase	0.001	-	-	-	-
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1
Moisture and miscellaneous	Up to 100%				
Minors include Brightener / SRP1 / CMC / Photobleach / MgSO4 / PVPVI/ Suds suppressor /PEG.					

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### Example 6

The following laundry compositions, which may be in the form of granules or tablet, were prepared in accordance with the invention:

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	3.0	3.0	1.0	3.0
MBAS 16.5, 1.9	4.0	2.0	4.0	2.0	4.0
LAS	4.0	-	4.0	-	3.0
C25AE3S	0.5	2.0	1.0	-	-
LAS/NaSKS-6	5.0	17.0	9.0	20.0	15.0
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	10.0	10.0	-	10.0
SKS-6	-	-	2.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0

	I	II	III	IV	V
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
PC	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.035	0.004	0.007	0.035	0.010
Amylase	0.003	0.003	0.006	0.010	0.008
Lipase	0.001	0.010	0.004	0.002	0.001
Cellulase	0.0008	0.0014	0.0003	0.001	0.001
Pectate lyase	0.001	0.02	0.01	0.015	0.03
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1

Moisture and miscellaneous Up to 100%

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO<sub>4</sub> / PVPVI/ Suds suppressor /PEG.

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### Example 7

The following granular detergent were prepared in accordance with the present invention:

	I	II	III	IV
Base granule				
STPP	-	22.0	-	15.0
Zeolite A	30.0	-	24.0	5.0
Sulfate	5.5	5.0	7.0	7.0
MA/AA	3.0	-	-	-

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76

	I	II	III	IV
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
MLAS	14.0	10.0	9.0	20.0
MBAS 16.5, 1.9	8.0	7.0	9.0	7.0
C45AE11S	-	1.0	-	1.0
MES	0.5	4.0	6.0	-
SADS	2.5	-	-	1.0
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	8.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
AO	1.0	0.5	0.5	0.5
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	13.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	0.033	0.033	0.033	0.0016
Lipase	0.008	-	-	0.008
Amylase	0.0016	-	-	0.0016
Cellulase	0.0002	0.0005	0.0005	0.0002
Pectate lyase	0.001	0.02	0.03	0.015
DTPA	0.5	0.3	0.5	1.0
PB1	5	3.0	10	4.0
NOBS/ TAED	0.5	0.3	0.5	0.6
Sulfate	4.0	5.0	-	5.0
SRP1	-	0.4	-	-
Sud supressor	-	0.5	-	-
speckle	0.9	-	2.7	1.2
Moisture and miscellaneous		Up to 100%		

		I	II	III
Agglomerate				
	QAS	2.0	-	1.0
	MES	-	2.0	-
	LAS	6.0	-	-
	TAS	-	2.0	-
	C45AS	6.0	2.0	1.0
	MBAS16.5, 1.9	4.0	2.0	2.0
	Zeolite A	15.0	6.0	-
	Carbonate	4.0	8.0	4.0
	MA/AA	4.0	2.0	-
	CMC	0.5	0.5	-
	DETPMP	0.4	0.4	-
Spray On				
	C25E3	1.0	1.0	-
	Perfume	0.5	0.5	0.5
Agglomerate				
	SKS-6	7.0	15.0	20.0
	LAS	5.8	9.0	15.0
	Zeolite	-	0.9	-
	C45 AS	-	3.0	-
	Water	0.08	0.1	-
Dry Adds				
	EDDS/HEDP	0.5	0.3	0.5
	NaSKS 6)	5.0	6.0	4.0
	Citrate	-	1.0	-
	Citric	2.0	-	2.0
	NAC OBS	4.1	-	5.0
	TAED	0.8	2.0	-
	Percarbonate	20.0	20.0	15.0

	I	II	III
SRP 1	0.3	0.3	-
Pectate lyase	0.01	0.02	0.001
Protease	0.046	0.046	0.033
Lipase	0.008	0.008	0.006
Cellulase	0.0014	0.0014	0.001
Amylase	0.004	0.004	-
QEA	1.0	-	1.0
Silicone antifoam	1.0	0.5	0.5
Brightener 1	0.2	0.2	-
Brightener 2	0.2	-	0.2
Density (g/litre)	850	850	800
Moisture and miscellaneous		Up to 100%	

Example 9

- 5 The following granular detergent were prepared in accordance with the present invention:

	I	II	III	IV
Base granule				
STPP	-	22.0	-	15.0
Zeolite A	30.0	-	24.0	5.0
Sulfate	5.5	5.0	7.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	10.0	7.0	6.0	15.0
C45AS	8.0	7.0	9.0	7.0
C45AE11S	-	1.0	-	1.0
MBAS 16.5, 1.9	4.0	3.0	3.0	5.0
MES	0.5	4.0	6.0	-
SADS	2.5	-	-	1.0
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2

	I	II	III	IV
Carbonate	6.0	9.0	8.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	13.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	0.033	0.033	0.033	0.0016
Lipase	0.008	-	-	0.008
Amylase	0.0016	-	-	0.0016
Cellulase	0.0002	0.0005	0.0005	0.0002
Pectate lyase	0.001	0.02	0.03	0.015
DTPA	0.5	0.3	0.5	1.0
PB1	5	3.0	10	4.0
NOBS/ TAED	0.5	0.3	0.5	0.6
Sulfate	4.0	5.0	-	5.0
SRP1	-	0.4	-	-
Sud supressor	-	0.5	-	-
speckle	0.9	-	2.7	1.2
Moisture and miscellaneous		Up to 100%		

Example 10

- 5 The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V
LAS	9.0	7.5	-	3.5	-
MLAS	2.0	1.0	-	-	-
AO	0.5	0.5	1.0	0.5	1.0

	I	II	III	IV	V
C25E2.5S	-	3.0	17.0	-	15.0
C45E2.25S	11.5	3.0	-	16.0	-
C23E9	-	3.0	2.0	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.0	-	3.0
TPKFA	2.0	-	2.0	0.5	2.0
Citric (50%)	6.5	1.0	2.5	4.0	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
SCS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	3.0
Na hydroxide	6.0	2.0	3.5	4.0	3.0
Ethanol	2.0	1.0	4.0	4.0	3.0
1,2 Propanediol	3.0	2.0	8.0	8.0	5.0
Monoethanolamine	3.0	1.5	1.0	2.5	1.0
TEPAE	2.0	-	1.0	1.0	1.0
Pectate lyase	0.001	0.002	0.01	0.01	0.005
Pectin lyase	0.001	0.001	-	-	-
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Miscellaneous and water					

#### Example 11

- 5 The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	I	II	III	IV
LAS	9.0	12.0	8.5	-	20.0	-	-	-
AO	1.0	1.0	0.5	2.0	5.0	3.0	1.0	1.0
MBAS 16.5, 1.9	2.0	0.5	1.0	4.0	-	4.0	10.0	4.0
C25AS	2.0	0.5	1.0	4.0	-	6.0	7.0	1.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl / tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rapeseed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	0.4	0.3
TEPAE	0.5	-	0.5	0.2	2.0	1.2	1.0	-
DETPMP	1.0	1.0	0.5	1.0				
Pectate lyase	0.01	.001	.001	0.02	0.02	.002	.002	0.02
Protease	0.02	0.02	0.01	.008	-	-	.003	.003
Lipase	-	.002	-	.002	.004	0.01	0.01	0.01
Amylase	.004	.004	0.01	.008	-	-	.004	.003
Cellulase	-	-	-	.002	-	-	.002	.001
SRP 2	0.3	-	0.3	0.1	1.0	1.5	2.5	2.5
Boric acid	0.1	0.2	1.0	2.0	4.0	4.0	-	-
Ca chloride	-	0.02	-	0.01	0.1	0.2	0.3	-
Brightener 1	-	0.4	-	-	0.4	-	-	-
Suds suppressor	0.1	0.3	-	0.1	0.8	0.7	-	-
Opacifier	0.5	0.4	-	0.3	8.0	7.5	8.0	8.2
NaOH up to pH	8.0	8.0	7.6	7.7				
Miscellaneous and water								

Example 12



The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V
LAS	9.0	6.0	-	4.0	-
C25E2.5S	-	3.0	15.0	-	10.0
C45E2.25S	9.0	3.0	-	10.0	-
MBAS 16.5, 1.9	5.0	3.0	3.0	6.0	6.0
C23E9	-	3.0	2.0	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.0	-	3.0
TPKFA	2.0	-	2.0	0.5	2.0
Citric (50%)	6.5	1.0	2.5	4.0	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
SCS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	3.0
Na hydroxide	6.0	2.0	3.5	4.0	3.0
Ethanol	2.0	1.0	4.0	4.0	3.0
1,2 Propanediol	3.0	2.0	8.0	8.0	5.0
Monoethanolamine	3.0	1.5	1.0	2.5	1.0
TEPAE	2.0	-	1.0	1.0	1.0
Pectate lyase	0.01	0.002	0.01	0.01	0.5
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
5 Miscellaneous and water					

### Example 13

The following liquid detergent compositions were prepared according to the present invention (Levels are given in parts by weight, enzyme are expressed in pure enzyme) :

5

	I	II
LAS	26.0	10.0
C45AS	12.0	6.0
C13E8	3.0	3.0
MBAS 16.5, 1.9	4.0	9.0
Oleic acid	3.0	2.5
Citric	5.0	5.0
Na hydroxide	0.4	4.0
Ca Formate	0.2	0.1
Na Formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	6.0	5.5
Xylene sulfonic acid	-	2.0
TEPAE	1.5	0.8
Protease	0.05	0.02
Pectate lyase	0.02	0.01
Pectin lyase	-	0.001
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume	0.5	0.3
Water and Minors		

### Example 14

10 The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	I	II	III	IV
LAS	5.0	9.0	6.0	-	20.0	-	-	-

	I	II	III	IV	I	II	III	IV
C25AS	4.0	1.0	2.0	6.0	-	6.0	10.0	10.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
MBAS 16.5, 1.9	5.0	5.0	3.0	4.0	5.0	7.0	8.0	5.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl / tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rapeseed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	0.4	0.3
TEPAE	0.5	-	0.5	0.2	2.0	1.2	1.0	-
DETPMP	1.0	1.0	0.5	1.0				
Pectate lyase	0.01	.001	.001	0.02	0.02	.002	.002	0.02
Protease	0.02	0.02	0.01	.008	-	-	.003	.003
Lipase	-	.002	-	.002	.004	0.01	0.01	0.01
Amylase	.004	.004	0.01	.008	-	-	.004	.003
Cellulase	-	-	-	.002	-	-	0.2	0.1
SRP 2	0.3	-	0.3	0.1	1.0	1.5	2.5	2.5
Boric acid	0.1	0.2	1.0	2.0	4.0	4.0	-	-
Ca chloride	-	0.02	-	0.01	0.1	0.2	0.3	-
Brightener 1	-	0.4	-	-	0.4	-	-	-
Suds suppressor	0.1	0.3	-	0.1	0.8	0.7	-	-
Opacifier	0.5	0.4	-	0.3	8.0	7.5	8.0	8.2
NaOH up to pH	8.0	8.0	7.6	7.7				
Miscellaneous and water								

#### Example 15

- The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV	V	VI	VII
LAS	10.0	10.0	17.0	16.0	15.0	15.0	12.0
C45AS		4.5	-		-	-	4.0
C45 E0.5S			-	-	-	-	-
C45 E3S	-	-	2.0	-	1.0	1.0	1.0
C45E6.5S	2.0	2.0	-	1.3	-	-	0.6
MBAS 16.5, 1.9	2.0	6.0	6.0	3.0	3.0	5.0	4.0
C <sub>9</sub> -C <sub>14</sub> alkyl dimethyl hydroxy ethyl quaternary ammonium salt			-	-	1.0	0.5	2.0
Tallow fatty acid			-	-	-	-	1.0
Tallow alcohol ethoxylate (50)	-	-	-	-	-	-	-
STPP	23.0	25.0	24.0	22.0	20.0	15.0	20.0
Carbonate	15.0	12.0	15.0	10.0	13.0	11.0	10.0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-
MA/AA	-	-	1.0	1.0	1.0	2.0	0.5
Silicate (1:6 ratio	3.0	6.0	9.0	8.0	9.0	6.0	8.0
Sulfate	25.0	18.0	20.0	18.0	20.0	22.0	13.0
PB1	5.0	5.0	10.0	8.0	3.0	1.0	2.0
PEG MW ~4000 (50%)	1.5	1.5	1.0	1.0	-	-	0.5
CMC	1.0	1.0	1.0	-	0.5	0.5	0.5
Citric	-	-	-	-	-	-	-
NOBS/ DOBS	0.5	1.0	0.5	0.5	1.0	0.7	0.3
TAED	1.5	1.0	2.5	3.0	0.3	0.2	0.5
SRP1	1.5	1.5	1.0	1.0	-	1.0	-
SRP2	-	-	-	-	1.0	-	1.0
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0
Mg sulphate	-	-	-	-	1.0	0.5	1.5
Chelant	-	-	-	-	0.8	0.6	1.0
Protease	0.035	0.004	0.007	0.035	0.010	0.010	0.007
Amylase	0.003	0.003	0.006	0.010	0.008	0.008	0.006
Lipase	0.001	0.010	0.004	0.002	0.001	0.001	0.004

	I	II	III	IV	V	VI	VII
Cellulase	.0008	.0014	.0003	0.001	0.001	0.001	.0003
Pectate lyase	0.001	0.02	0.01	0.001	0.002	0.015	0.03
speckle	2.5	4.1	4.2	4.4	5.6	5.0	5.2
Minors	1.0	1.0	1.0	1.0	0.5	1.5	1.0

Example 16

The following granular fabric detergent compositions which provide "softening  
5 through the wash" capability were prepared according to the present invention :

	I	II	III	IV
C45AS	-	8.0	-	4.0
LAS	5.0	-	2.0	-
MBAS 16.5, 1.9	2.6	2.0	-	-
AO	-	-	2.6	2.0
C68AS	1.3	-	1.3	-
C45E7	4.0	-	4.0	-
C25E3	-	5.0	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0	1.4	1.0
Citrate	5.0	3.0	5.0	3.0
Na-SKS-6	-	11.0	-	11.0
Zeolite A	15.0	15.0	15.0	15.0
MA/AA	4.0	4.0	4.0	4.0
DETPMP	0.4	0.4	0.4	0.4
PB1	15.0	-	15.0	-
Percarbonate	-	15.0	-	15.0
TAED	5.0	5.0	5.0	5.0
Smectite clay	10.0	10.0	10.0	10.0
HMWPEO	-	0.1	-	0.1
Pectate lyase	0.001	0.01	0.001	0.01
Protease	0.02	0.01	0.02	0.01
Lipase	0.02	0.01	0.02	0.01
Amylase	0.03	0.005	0.03	0.005
Cellulase	0.001	-	0.001	-

	I	II	III	IV
Silicate	3.0	5.0	3.0	5.0
Carbonate	10.0	10.0	10.0	10.0
Suds suppressor	1.0	4.0	1.0	4.0
CMC	0.2	0.1	0.2	0.1
Miscellaneous and minors		Up to 100%		

### Example 17

- 5 The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV
LAS	10.3	12.0	8.0	5.0
C45 AS	3.9	4.0	4.5	-
C45 E0.5S	2.0	2.0	-	-
C45 E3S	-	-	-	-
C45E6.5S	0.5	0.5	0.5	5.0
MBAS 16.5, 1.9	3.0	1.7	2.4	3.0
C <sub>9</sub> -C <sub>14</sub> alkyl dimethyl hydroxy ethyl quaternary ammonium salt	1.0	-	-	0.5
Tallow fatty acid	0.5	-	-	-
Tallow alcohol ethoxylate (50)	-	-	1.0	0.3
STPP	-	41.0	-	20.0
Zeolite A	26.3	-	21.3	1.0
Carbonate	23.9	12.4	25.2	17.0
Sodium Polyacrylate (45%)	3.4	0.0	2.7	-
MA/AA	-	-	1.0	1.5
Silicate (1:6 ratio)	2.4	6.4	2.1	6.0
Sulfate	10.5	10.9	8.2	15.0
PB1	1.0	1.0	1.0	2.0
PEG MW ~4000 (50%)	1.7	0.4	1.0	-
CMC	1.0	-	-	0.3
Citric	-	-	3.0	-
NOBS/ DOBS	0.2	0.5	0.5	0.1
TAED	0.6	0.5	0.4	0.3

	I	II	III	IV
SRP 1	1.5	-	-	-
SRP2	-	1.5	1.0	1.0
Moisture	7.5	3.1	6.1	7.3
Mn sulphate	-	-	-	1.0
Chelant	-	-	-	0.5
speckles	0.5	1.0	3.0	0.5
Pectate lyase	0.001	0.01	0.005	0.002
Protease	0.035	0.004	0.007	0.035
Amylase	0.003	0.003	0.006	0.010
Lipase	0.001	0.010	0.004	0.002
Cellulase	0.0008	0.0014	0.0003	0.001
Minors	1.0	1.0	1.0	1.0

Example 18

- 5 The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	VI	V	III	VI	V
LAS	-	-	18.0	10.0	18.0	5.75	5.8	-
C28AS	25.0	12.5	-	-	-	14.75	11.2	19.0
MBAS 16.5, 1.9	5.0	1.0	1.0	5.0	3.0	2.0	3.0	3.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-

	I	II	III	IV	V	VI	VII
C12-14E06-2S	23.0	25.0	24.0	28.0	18.0	23.0	24.0
C12-14 alkyl dimethyl amine oxide	2.0	6.0	6.0	7.8	5.0	6.0	6.0
MBAS 16.5, 1.9	2.0	3.0	2.0	2.0	2.0	3.0	2.0
C12-14 alkyl dimethyl betaine	2.0	-	-	-	-	-	-
C12-14 glucose amide	3.0	1.0	-	-	-	-	-
C11EO9	-	1.0	-	4.0	2.0	-	-
C9-11EO8	5.0	-	3.0	-	-	3.0	3.0
DTPA	-	0.1	-	-	-	-	-
SCS	-	1.0	3.5	3.0	2.5	3.5	3.5
Xylene sulfonate	-	3.0	-	-	-	-	-



	I	II	III	IV	V
Pectate lyase	0.005	0.001	0.02	0.02	0.005
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
AO	0.5	0.5	0.5	0.5	0.5
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-
LAS	0.5	0.5	0.5	-	-
C12 AS	0.5	0.5	0.5	-	-

	I	II	III	IV	V
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12,13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Neodol 23-3	-	-	-	-	1.5
Neodol 91-10	-	-	-	-	1.6
C25AE1.8S	-	-	-	6.0	
Na paraffin sulphonate	-	-	-	6.0	
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	
Ethoxylated tetraethylene pentaime	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water	Up to 100%				
*Na4 ethylenediamine diacetic acid					
**Diethylene glycol monohexyl ether					

5

Example 21

The following liquid hard surface cleaning compositions were prepared according to the present invention :

	I	II	III	IV	V
Pectate lyase	0.005	0.001	0.02	0.02	0.005
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	0.5	-

Pectate lyase	0.01
Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	3.0
MBAS 16.5, 1.9	1.0
Na hydroxide	0.8

Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%
*Diethylene glycol monobutyl ether	

### Example 23

- 5 The following disinfecting compositions were prepared according to the present invention.

	I	II	III	IV	V
	Wipe	Wipe	Spray	Liquid	Liquid
H2O2	1.0	1.0	1.5	1.0	1.0
Na tetraborate 10.H2O	-	-	1.0	-	-
C10 Amine Oxide	-	-	0.9	0.9	0.9
C12-14 alkyl dimethyl amine oxide	0.4	0.4	-	-	-
MBAS 16.5, 1.9	0.5	-	0.5	0.5	0.5
C7-10 AS	-	-	-	6.0	6.0
C9-11EO10	-	-	0.05	-	-
C8-18 Fatty acid	-	-	0.1	0.2	0.2
AO	-	0.5	-	-	0.5
Ethanol	9.0	9.0	1.0	2.5	2.5
Benzyl alcohol	-	-	0.8	-	-
Propylene or diethylene glycol butyl ether	1.0	1.0	1.5	-	-
Poly(propylene glycol) monobutyl ether	0.2	0.2	-	-	-
HEDP	-	-	0.1	-	-
Butylated hydroxytoluene	0.01	0.01	0.06	0.03	0.03
Salicyclic acid	0.03	0.03	-	0.07	0.07
Pectate lyase	0.001	0.001	0.01	0.005	0.005
Perfume	0.1	0.1	0.3	0.3	0.3
Citric	0.7	0.7	-	1.5	1.5
Dye	-	-	-	2.0	2.0
NaOH	-	-	0.1	-	-

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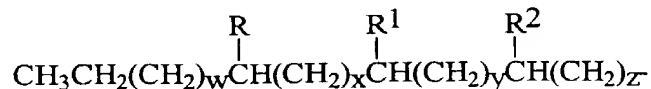
94

Miscellaneous and water

Up to 100%

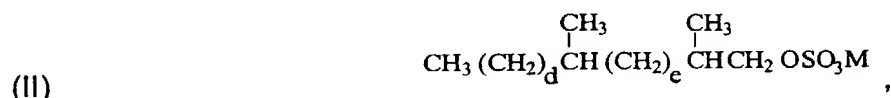
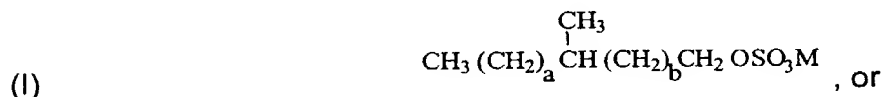
- (III) X is selected from  $-\text{CH}_2-$  and  $-\text{C}(\text{O})-$ .

2. A detergent composition according to claim 1 wherein said mid-chain branched anionic surfactant is of the above formula wherein the A<sup>b</sup> moiety is a branched primary alkyl moiety having the formula:



wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula, including the R, R<sup>1</sup>, and R<sup>2</sup> branching, is from 13 to 19; R, R<sup>1</sup>, and R<sup>2</sup> are each independently selected from hydrogen and C<sub>1</sub>-C<sub>3</sub> alkyl, preferably methyl, provided R, R<sup>1</sup>, and R<sup>2</sup> are not all hydrogen and, when z is 0, at least R or R<sup>1</sup> is not hydrogen; w is an integer from 0 to 13; x is an integer from 0 to 13; y is an integer from 0 to 13; z is an integer from 0 to 13; and w + x + y + z is from 7 to 13.

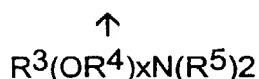
3. A detergent composition according to claims 1-2 wherein said mid-chain branched anionic surfactant has the formula:



or mixtures thereof; wherein M represents one or more cations; a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8; when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9; when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10; when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11; when a + b = 14, a is an integer from 2 to 13 and b is an integer from 1 to 12; when a + b = 15, a is an integer from 2 to 14 and b is an integer from 1 to 13; when a + b = 16, a is an integer from 2 to 15 and b is an integer from 1 to 14; when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6; when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7; when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8; when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9;

when  $d + e = 12$ ,  $d$  is an integer from 2 to 11 and  $e$  is an integer from 1 to 10;  
 when  $d + e = 13$ ,  $d$  is an integer from 2 to 12 and  $e$  is an integer from 1 to 11;  
 when  $d + e = 14$ ,  $d$  is an integer from 2 to 13 and  $e$  is an integer from 1 to 12;  
 whereby, when more than one of these sulfate surfactants is present in the  
 surfactant system, the average total number of carbon atoms in the  
 branched primary alkyl moieties is from 11 to 20, preferably 14.5 to 18.

4. A detergent composition according to claims 1-3 wherein said mid-chain  
 branched anionic surfactant has an  $A^b - X$  moiety comprising from 11 to 20,  
 preferably 16 to 18 carbon atoms and  $B$  is a sulfate group.
5. A detergent composition according to claims 1-4 wherein said amine oxide  
 surfactant is of the formula



wherein  $R^3$  is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures  
 thereof containing from about 8 to about 22 carbon atoms;  $R^4$  is an  
 alkylene or hydroxyalkylene group containing from about 2 to about 3  
 carbon atoms or mixtures thereof;  $x$  is from 0 to about 3; and each  $R^5$  is an  
 alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms  
 or a polyethylene oxide group containing from about 1 to about 3 ethylene  
 oxide groups. The  $R^5$  groups can be attached to each other, e.g., through  
 an oxygen or nitrogen atom, to form a ring structure.

6. A detergent composition according to claims 1-5 wherein said amine oxide  
 surfactant is selected from  $C_{10}$ - $C_{18}$  alkyl dimethyl amine oxides;  $C_8$ - $C_{12}$   
 alkoxy ethyl dihydroxy ethyl amine oxides and/or mixtures thereof.
7. A detergent composition according to claims 1-6 wherein said amine oxide  
 surfactant is comprised at a level of from 0.2% to 15%, preferably from 1%  
 to 10%, more preferably less than 5% by weight of total composition.
8. A detergent composition according to claims 1-7 wherein said mid-chain  
 branched anionic surfactant is comprised at a level of from 0.1% to 50%,



preferably from 0.5% to 40%, more preferably 1% to 35% by weight of the total composition.

- 5 9. A detergent composition according to any of the preceding claims wherein said pectate lyase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.02% pure enzyme by weight of total composition.
- 10 10. A detergent composition according to any of the present invention further comprising a pectin lyase enzyme.
- 15 11. A method of cleaning a fabric, a dishware or hard surface with a detergent composition according to any of the preceding claims, for superior cleaning performance.

  
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C11D 3/386, 1/02, 1/75, 1/83</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/42155</b> <b>(43) International Publication Date:</b> 20 July 2000 (20.07.00)												
<b>(21) International Application Number:</b> PCT/US00/00794 <b>(22) International Filing Date:</b> 13 January 2000 (13.01.00)  <b>(30) Priority Data:</b> <table border="0" style="width: 100%;"><tr><td style="width: 40%;">PCT/US99/00797</td><td style="width: 40%;">14 January 1999 (14.01.99)</td><td style="width: 20%;">US</td></tr><tr><td>PCT/US99/00800</td><td>14 January 1999 (14.01.99)</td><td>US</td></tr><tr><td>PCT/US99/00806</td><td>14 January 1999 (14.01.99)</td><td>US</td></tr><tr><td>PCT/US99/00790</td><td>14 January 1999 (14.01.99)</td><td>US</td></tr></table> <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SHOWELL, Michael, Stanford [US/US]; 685 Compton Road, Cincinnati, OH 45231 (US). ZHU, Yong [CN/US]; 4348 Bromyard Avenue, Cincinnati, OH 45241 (US). BETTIOL, Jean-Luc, Philippe [FR/BE]; 93 Avenue Slegers, B-1200 Brussels, Belgium (BE). WELLS, Eric, C. [US/US]; 1440 W. Kemper Road #1601, Cincinnati, OH 45240 (US). MOESE, Rosa, Laura [US/US]; 8815 Eagle Creek Court, West Chester, OH 45069 (US). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B-1840 Londerzeel (BE).		PCT/US99/00797	14 January 1999 (14.01.99)	US	PCT/US99/00800	14 January 1999 (14.01.99)	US	PCT/US99/00806	14 January 1999 (14.01.99)	US	PCT/US99/00790	14 January 1999 (14.01.99)	US	<b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).  <b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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PCT/US99/00790	14 January 1999 (14.01.99)	US												
<b>(54) Title:</b> DETERGENT COMPOSITIONS COMPRISING A PECTATE LYASE AND A SPECIFIC SURFACTANT SYSTEM  <b>(57) Abstract</b> <p>The present invention relates to detergent compositions comprising a pectate lyase and surfactant selected from a mid-chain branched anionic surfactant and/or an amine oxide surfactant, for superior cleaning performance.</p>														



## DECLARATION COMBINED WITH POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"Detergent Compositions Comprising a Pectate Lyase and a Specific Surfactant"

bearing the above listed Procter & Gamble Company Case number, the specification of which was filed as PCT/US00/00794, designating at least the United States of America, with the United States Receiving Office on 13 January 2000.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37 Code of Federal Regulations §1.56.

I hereby claim foreign priority benefits under Title 35 United States Code §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application for patent or Inventor's certificate having a filing date before that of the application on which priority is claimed:

## PRIOR FOREIGN APPLICATION(S) TO WHICH WE CLAIM PRIORITY:

PCT/US99/00797		14 January 1999
PCT/US99/00800	PCT	14 January 1999
PCT/US99/00806	PCT	14 January 1999
PCT/US99/00790	PCT	14 January 1999

I hereby claim the benefit under Title 35 United States Code §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

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(Appln. Serial No.)	(Filing Date)	(Status)(patented, pending, abandoned)

I hereby appoint the following as my attorney(s) or agent(s) with full power of substitution to prosecute this application and transact all business in the Patent and Trademark office connected therewith:

Name	Registration No.	Associate Power of Attorney Attached [ ] Yes [ ] No
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